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NCERT Exemplar Solutions

Complete Set — All 77 Solved NCERT Exemplar Problems for Class 12 Chemistry, Chapter 9 (Syllabus 2026-27)

Chapter 9: Amines

About this Chapter

Amines are nitrogen-containing organic bases derived conceptually from NH_3 by replacing one, two, or three H atoms with alkyl or aryl groups, giving **primary** ($R-NH_2$), **secondary** (R_2NH) and **tertiary** (R_3N) amines. This Exemplar set drills the key concepts: classification and nomenclature, preparation via ammonolysis, Gabriel phthalimide synthesis, Hoffmann bromamide degradation, reduction of nitriles/nitro/amides, basicity trends (gas vs. aqueous phase, aliphatic vs. aromatic), reactions with HNO_2, diazotisation, Sandmeyer/azo coupling, the Hinsberg test and the carbylamine test that JEE/NEET papers keep asking.

Topics covered: Structure & classification • IUPAC nomenclature • Preparation (ammonolysis, Gabriel, Hoffmann, reduction) • Basicity (pK_b) trends • Acylation, alkylation • Reaction with HNO_2 • Diazonium salts, Sandmeyer, azo coupling • Hinsberg & carbylamine tests

Quick Formula Sheet

Basicity (aqueous, aliphatic):

$2^\circ > 1^\circ \approx 3^\circ > NH_3$

Basicity (gas phase):

$3^\circ > 2^\circ > 1^\circ > NH_3$

Aniline vs. alkyl amine:

$R-NH_2 > NH_3 > Ar-NH_2$

Gabriel:

$$Phth-N^- K^+ + R-X \longrightarrow Phth-N-R \xrightarrow{H_3O^+} R-NH_2$$

Hoffmann bromamide:

$$R-CONH_2 \xrightarrow{Br_2/NaOH} R-NH_2 \ (-1\ C)$$

Sandmeyer:

$$ArN_2^+ \xrightarrow{CuX} Ar-X + N_2$$

I. Multiple Choice Questions (Type-I)

Q 9.1 **Which of the following is a 3° amine?**

(i) 1-methylcyclohexylamine (ii) Triethylamine

(iii) *tert*-butylamine (iv) N-methylaniline

SOLUTION

Correct option: (ii) Triethylamine, $(C_2H_5)_3N$.

Concept used. An amine's **degree** is decided by how many *carbon* substituents sit on the nitrogen, not by the carbon skeleton. 1° has one $C-N$ bond, 2° has two, and 3° has three. The classification of the carbon bearing $-NH_2$ (e.g. *tert*-butyl) is irrelevant for amine ordering.

Step 1. (i) 1-methylcyclohexylamine: $-NH_2$ on a ring carbon $\Rightarrow$ only one $C-N$ bond $\Rightarrow$ 1°.

Step 2. (ii) Triethylamine $N(C_2H_5)_3$: three ethyl groups on N $\Rightarrow$ 3°.

Step 3. (iii) $tert$-butylamine $(CH_3)_3C-NH_2$: still only one $C-N$ bond $\Rightarrow$ 1° (the carbon is 3°, not the amine).

Step 4. (iv) N-methylaniline $C_6H_5-NH-CH_3$: two $C-N$ bonds $\Rightarrow$ 2°.

Final Answer: Only triethylamine has three carbons on N; option **(ii)**.

✗ Don't be fooled by "tert"!

"$tert$-butylamine" looks tertiary but is 1° — "tert" describes the *carbon*, not the *amine*. Count $C-N$ bonds only.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Count-the-carbons angle. The cleanest discrimination here is a one-step inspection: cover everything except the nitrogen atom and count carbons bonded *directly* to N. The labels "methyl", "cyclohexyl" or "*tert*-butyl" on neighbouring carbons are noise — only $C-N$ bonds set the amine class.

Run the count on each option. (i) 1-methylcyclohexylamine: a single ring carbon carries NH_2, so N touches one carbon $\Rightarrow$ 1°. (ii) Triethylamine $N(C_2H_5)_3$: N holds three ethyl groups, three $C-N$ bonds $\Rightarrow$ 3°. (iii) *tert*-butylamine $(CH_3)_3C-NH_2$: the carbon is 3° but the nitrogen still sees only one C $\Rightarrow$ 1°. (iv) N-methylaniline $C_6H_5-NHCH_3$: two carbons on N $\Rightarrow$ 2°. Only triethylamine clears the three-carbon bar.

Final Answer: Triethylamine; option **(ii)**.

Q 9.2 **The correct IUPAC name for $CH_2=CHCH_2NHCH_3$ is _____.**

(i) Allylmethylamine (ii) 2-amino-4-pentene

(iii) 4-aminopent-1-ene (iv) N-methylprop-2-en-1-amine

SOLUTION

Correct option: (iv) N-methylprop-2-en-1-amine.

Concept used. For an amine, the IUPAC name is built from the longest carbon chain bearing $-NH-$ (or $-NH_2$), numbered so that the amine carbon takes the lowest locant. Any group on N is indicated by an italic "N-" prefix. Double bonds get their own locant ("-en-").

Step 1. Parent chain: the three-carbon $CH_2{=}CH{-}CH_2{}^-$ piece (the N is attached to C-1, the $=CH^-$ to C-2).

Step 2. Suffix: "-amine" on C-1 $\Rightarrow$ "prop-2-en-1-amine".

Step 3. Substituent on N: $-CH_3 \Rightarrow$ prefix "N-methyl".

Step 4. Full name: N-methylprop-2-en-1-amine. The common name "allylmethylamine" is non-IUPAC.

Final Answer: N-methylprop-2-en-1-amine; option **(iv)**.

☞ **Why not "4-aminopent-1-ene"**

That name would belong to a 5-carbon chain ($CH_2{=}CH{-}CH_2{-}CH(NH_2){-}CH_3$), not the structure given. Always count carbons in the chain that includes the amine carbon.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Build-the-name angle. Draw the connectivity first: a three-carbon chain $CH_2{=}CH{-}CH_2{}^-$ with $NH(CH_3)$ on its terminal carbon. The parent must be the longest chain that contains the amine carbon, which is the three-carbon "propene" chain. The amine is on C-1 and the double bond is between C-2 and C-3 when numbered from the amine end, so the parent name is prop-2-en-1-amine. The methyl group hanging off the nitrogen is denoted with the locant "N-", giving the full name N-methylprop-2-en-1-amine.

Final Answer: Option **(iv)**.

Q 9.3 **Amongst the following, the strongest base in aqueous medium is _____.**

(i) CH_3NH_2 **(ii)** $NCCH_2NH_2$ **(iii)** $(CH_3)_2NH$ **(iv)** $C_6H_5NHCH_3$

SOLUTION

Correct option: (iii) $(CH_3)_2NH$, dimethylamine.
Concept used. In aqueous medium the strongest base combines **electron-donating** alkyl groups (raise lone-pair availability) with good **hydration** of the conjugate ammonium ion. 2° aliphatic amines balance these factors best, giving the well-known order $2^\circ > 1^\circ \approx 3^\circ > NH_3 \gg$ aryl amines.

Step 1. (i) CH_3NH_2: one $+I$ methyl $\Rightarrow$ moderately basic.

Step 2. (ii) $NCCH_2NH_2$: $-C{\equiv}N$ is strongly $-I$ $\Rightarrow$ withdraws density off N $\Rightarrow$ weak base.

Step 3. (iii) $(CH_3)_2NH$: two $+I$ methyls + two $N-H$ bonds still solvate the ammonium ion well $\Rightarrow$ strongest.

Step 4. (iv) $C_6H_5NHCH_3$: lone pair on N delocalises into the ring $\Rightarrow$ aryl amine, weakest of the four.

Final Answer: $(CH_3)_2NH$ is the strongest aqueous base; option **(iii)**.

☞ **Aqueous basicity order**
$(CH_3)_2NH > CH_3NH_2 \approx (CH_3)_3N > NH_3 > C_6H_5NH_2$ — two methyls win in water.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Eliminate-the-bad angle. Two of the four options eliminate themselves on sight. Option (ii) carries an $-C{\equiv}N$ group: cyano is one of the most strongly $-I$ substituents and pulls density straight off the nitrogen lone pair $\Rightarrow$ very weak base. Option (iv) is an aromatic amine: the nitrogen lone pair conjugates into the benzene ring, leaving little density for H^+ acceptance — weaker than even ammonia.
Between (i) and (iii) the deciding factors are inductive donation and aqueous solvation. Dimethylamine has two $+I$ methyl groups *plus* two residual $N-H$ bonds that the conjugate $(CH_3)_2NH_2{}^+$ uses for hydrogen-bond solvation. That combination beats methylamine (one methyl, three solvating $N-H$) on inductive contribution and beats trimethylamine on solvation. Hence dimethylamine sits at the top of the aqueous basicity ladder among these four.

Final Answer: Option **(iii)** $(CH_3)_2NH$.

Q 9.4 Which of the following is the weakest Brönsted base?

(i) Aniline ($C_6H_5-NH_2$) (ii) Piperidine (cyclic 2° amine $C_5H_{10}NH$)

(iii) Cyclohexylamine (iv) CH_3NH_2

SOLUTION

Correct option: (i) Aniline.

Concept used. Brønsted basicity of an amine is set by how available the N lone pair is for protonation. Aromatic amines like aniline drain the lone pair into the ring by resonance $\Rightarrow$ much weaker base than alkylamines (where the lone pair is fully localised on N and is reinforced by $+I$).

Step 1. Aniline: lone pair on N overlaps with the benzene ring; four resonance structures put N^+ on the ring $\Rightarrow$ lone pair is partly delocalised, basicity low ($pK_b \approx 9.4$).

Step 2. Piperidine ($pK_b \approx 2.9$): cyclic 2° aliphatic amine, very strong base.

Step 3. Cyclohexylamine ($pK_b \approx 3.4$): strong $+I$ from cyclohexyl, strong base.

Step 4. Methylamine ($pK_b \approx 3.4$): one $+I$ methyl, moderately strong.

Final Answer: Aniline is the weakest Brönsted base among the four; option **(i)**.

☞ **Spot the aromatic amine first**

Whenever an MCQ pits one $Ar-NH_2$ against alkylamines, the aryl amine is almost always the weakest base in the set — resonance into the ring beats every inductive donor.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Sort-by-class angle. Group the four amines into "aromatic" (lone pair conjugated with a ring) versus "aliphatic" (lone pair localised on N). Only aniline sits in the aromatic bucket; piperidine, cyclohexylamine and methylamine are all aliphatic. The aromatic bucket loses about five pK_b units of basicity to lone-pair delocalisation into the ring, so aniline ($pK_b \approx 9.4$) is already an order of magnitude or more weaker than any of the three aliphatic amines on this list. The answer is therefore aniline without needing finer discrimination among the aliphatic three.

Final Answer: Option **(i)** aniline.

Q 9.5 Benzylamine may be alkylated as

$$C_6H_5CH_2NH_2 + R-X \longrightarrow C_6H_5CH_2NHR.$$

Which of the following alkyl halides is best suited for this reaction through S_N1 mechanism?

(i) CH_3Br **(ii)** C_6H_5Br **(iii)** $C_6H_5CH_2Br$ **(iv)** C_2H_5Br

SOLUTION

Correct option: (iii) $C_6H_5CH_2Br$ (benzyl bromide).

Concept used. S_N1 proceeds through a **carbocation**. The reaction rate scales with the stability of that cation: *resonance-stabilised* cations (benzyl, allyl) and $3^\circ > 2^\circ$ alkyl cations win; aryl halides cannot do S_N1 because phenyl cations are extremely unstable.

Step 1. (i) CH_3-X and (iv) C_2H_5-X: primary alkyl halides $\Rightarrow$ cation is CH_3^+ or $C_2H_5^+$, both highly unstable $\Rightarrow$ S_N1 does not run; S_N2 pathway only.

Step 2. (ii) C_6H_5-Br: aryl halide; the $C-Br$ bond is sp^2, S_N1 would require a phenyl cation $\Rightarrow$ impossible.

Step 3. (iii) $C_6H_5CH_2-Br$: ionises to the resonance-stabilised benzylic cation $C_6H_5-CH_2^+$ $\Rightarrow$ excellent S_N1 substrate.

Final Answer: Benzyl bromide; option **(iii)**.

☞ **Benzylic cation stability**

The benzylic cation $C_6H_5-CH_2^+$ is stabilised by four resonance contributors that delocalise the positive charge onto the o, o', p carbons of the ring — comparable to a 3° aliphatic cation.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Cation-stability angle. S_N1 rate is set by how fast the alkyl halide ionises to a carbocation, which in turn is set by how stable that cation is. Methyl and ethyl bromide would have to give CH_3^+ and $CH_3CH_2^+$ — both primary cations of unusable stability, ruling out S_N1. Bromobenzene cannot ionise at all because a phenyl cation $C_6H_5^+$ has no stabilising hyperconjugation and a vacant orbital on sp^2 carbon. Benzyl bromide, in contrast, ionises to the benzylic cation that spreads its positive charge over the ring via four canonical resonance structures, mimicking a tertiary cation in stability. So benzyl bromide is the only S_N1-friendly halide in the list.

Final Answer: Option **(iii)** $C_6H_5CH_2Br$.

Q 9.6 **Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine?**

(i) H_2 **(excess)/Pt (ii)** $LiAlH_4$ **in ether**

(iii) Fe and HCl (iv) Sn and HCl

SOLUTION

Correct option: (ii) $LiAlH_4$ in ether.

Concept used. Aryl nitro compounds $Ar-NO_2$ are reduced to aryl amines $Ar-NH_2$ by **dissolving-metal** reductants in acidic medium (Sn/HCl, Fe/HCl), or by catalytic hydrogenation (H_2/Pt, Pd, Ni). $LiAlH_4$ is unsuitable: with aromatic nitro groups it tends to stop at **azo** ($Ar-N=N-Ar$) or **hydrazo** ($Ar-NH-NH-Ar$) compounds rather than going cleanly to $Ar-NH_2$.

Step 1. Acidic dissolving-metal:
$$Ar-NO_2 + 3\,Sn + 7\,HCl \longrightarrow Ar-NH_3{}^+\,Cl^- + 3\,SnCl_2 + 2\,H_2O.$$

Step 2. Catalytic hydrogenation over Pt: $Ar-NO_2 + 3\,H_2 \longrightarrow Ar-NH_2 + 2\,H_2O$.

Step 3. $LiAlH_4$ delivers H^- but does not cleanly cleave the second $N-O$ bond on an aryl nitro group; product mixtures (azo/hydrazo) result.

> **Final Answer:** $LiAlH_4$ is the poor choice; option **(ii)**.

☞ **Reagent shortlist for $Ar-NO_2 \longrightarrow Ar-NH_2$**

Sn/HCl, Fe/HCl, Zn/HCl, H_2/Pt-Pd-Ni, $NaBH_4/NiCl_2$. Avoid $LiAlH_4$.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Pattern-recognition angle. The CBSE/NCERT textbook lists exactly three "approved" routes from $Ar-NO_2$ to $Ar-NH_2$: acidic dissolving-metal (Sn/HCl or Fe/HCl), and catalytic H_2 over Pt/Pd/Ni. Anything outside that triad is the odd one out, and here that role is filled by $LiAlH_4$ in ether.

The chemical reason is that aromatic nitro groups are π-conjugated with the ring, so simple hydride delivery stalls at intermediate stages — azoxy, azo and hydrazo species (coloured by-products). Acidic conditions provide protons that keep funnelling the intermediates onward; catalytic hydrogen provides clean surface reduction. $LiAlH_4$ provides neither a proton bath nor a metal surface, so the reduction tarballs.

> **Final Answer:** Option **(ii)** $LiAlH_4$/ether is the wrong reagent.

Q 9.7 **In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as source of nitrogen is _____.**

(i) Sodium amide, $NaNH_2$ **(ii) Sodium azide,** NaN_3

(iii) Potassium cyanide, KCN (iv) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

SOLUTION

Correct option: (iii) Potassium cyanide (KCN).

Concept used. To add *one* carbon while installing a 1° amine, the standard route is $\mathrm{R{-}X} \xrightarrow{\mathrm{KCN}} \mathrm{R{-}CN} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{R{-}CH_2{-}NH_2}$. The nitrile carbon becomes the new $-\mathrm{CH_2}-$ in the amine. The other reagents give amines but with no chain extension.

Step 1. $\mathrm{R{-}X + KCN \longrightarrow R{-}CN + KX}$ ($\mathrm{S_N2}$).

Step 2. $\mathrm{R{-}CN + 4\,[H]} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{R{-}CH_2{-}NH_2}$ (one C added as the new $-\mathrm{CH_2}-$ next to N).

Step 3. $\mathrm{NaNH_2}$ would just deprotonate or give nitrene; $\mathrm{NaN_3}$ gives $\mathrm{R{-}N_3} \longrightarrow \mathrm{R{-}NH_2}$ with *no* chain extension; phthalimide (Gabriel) gives $\mathrm{R{-}NH_2}$ also with *no* chain extension.

Final Answer: KCN; option **(iii)**.

☞ Chain-length checklist for amine synthesis

• Same C: Gabriel ($\mathrm{Phth{-}NK/R{-}X}$), azide ($\mathrm{NaN_3/R{-}X}$), ammonolysis ($\mathrm{NH_3/R{-}X}$). • $+1$ C: nitrile route ($\mathrm{KCN/R{-}X}$ then $\mathrm{LiAlH_4}$). • -1 C: Hoffmann bromamide ($\mathrm{R{-}CONH_2}$ + $\mathrm{Br_2/NaOH}$).

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Match-the-constraint angle. The question demands two things simultaneously — the product is a primary amine, and the carbon chain must grow by one $\mathrm{CH_2}$. Only the nitrile route does both: KCN first delivers $-\mathrm{CN}$ onto $\mathrm{R{-}X}$ via $\mathrm{S_N2}$, then catalytic or hydride reduction (Pt/Pd or $\mathrm{LiAlH_4}$) of $\mathrm{R{-}CN}$ adds two hydrogens at carbon and two at nitrogen to give $\mathrm{R{-}CH_2{-}NH_2}$. The freshly installed $\mathrm{CH_2}$ comes from the nitrile carbon, so the chain is one carbon longer than the parent halide. The other three reagents either keep the chain length the same (azide, phthalimide) or fail to give a primary amine at all (sodium amide).

Final Answer: KCN; option **(iii)**.

Q 9.8 **The source of nitrogen in Gabriel synthesis of amines is _____.**

(i) Sodium azide, $\mathrm{NaN_3}$ **(ii) Sodium nitrite,** $\mathrm{NaNO_2}$

(iii) Potassium cyanide, KCN **(iv) Potassium phthalimide,** $\mathrm{C_6H_4(CO)_2N^-K^+}$

SOLUTION

Correct option: (iv) Potassium phthalimide.

Concept used. **Gabriel synthesis** converts a 1° alkyl halide into a pure 1° amine without over-alkylation. The nitrogen source is potassium phthalimide, made by reacting phthalimide with KOH. Its anion $\mathrm{Phth{-}N^-}$ does $\mathrm{S_N2}$ on $\mathrm{R{-}X}$; subsequent acid or base hydrolysis releases $\mathrm{R{-}NH_2}$ plus phthalic acid.

Step 1. Deprotonation of phthalimide with KOH:

$$\mathrm{Phth{-}NH + KOH \longrightarrow Phth{-}N^-\,K^+ + H_2O}$$

Step 2. Alkylation by $\mathrm{S_N2}$:

$$\mathrm{Phth{-}N^-\,K^+ + R{-}X \longrightarrow Phth{-}N{-}R + KX}$$

Step 3. Hydrolysis with aqueous acid:

$$\mathrm{Phth{-}N{-}R + H_3O^+ \longrightarrow R{-}NH_2 + \text{phthalic acid}}$$

(hydrazine $\mathrm{NH_2NH_2}$ gives the same amine plus phthalhydrazide as the by-product).

Final Answer: Nitrogen comes from potassium phthalimide; option **(iv)**.

☞ **Why Gabriel beats ammonolysis**

Plain $\mathrm{NH_3 + R{-}X}$ over-alkylates ($\rightarrow$ mix of $1^\circ/2^\circ/3^\circ/4^\circ$). Phthalimide-N has only one acidic H, so only one alkylation can occur $\Rightarrow$ pure 1° amine.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Definition-first angle. "Gabriel" literally names the phthalimide route to primary amines, so the only acceptable nitrogen donor is potassium phthalimide. The other three reagents are the headline N-sources for sibling syntheses — sodium azide is the azide synthesis (gives $\mathrm{R{-}N_3}$, then $\mathrm{R{-}NH_2}$ after reduction), $\mathrm{NaNO_2}$ is the diazotisation reagent and KCN is the nitrile route (gives $\mathrm{R{-}CN}$, then $\mathrm{R{-}CH_2{-}NH_2}$ on $\mathrm{LiAlH_4}$ reduction — the chain grows by one carbon).

Final Answer: Potassium phthalimide; option **(iv)**.

Q 9.9 **Amongst the given set of reactants, the most appropriate for preparing 2° amine is _____.**

(i) 2° $R-Br + NH_3$ **(ii)** 2° $R-Br + NaCN$ **followed by** H_2/Pt
(iii) 1° $R-NH_2 + RCHO$ **followed by** H_2/Pt
(iv) 1° $R-Br$ **(2 mol) + potassium phthalimide followed by** $H_3O^+/heat$

SOLUTION

Correct option: (iii) reductive amination of a 1° amine with an aldehyde.
Concept used. **Reductive amination** is the cleanest laboratory route to 2° amines: a 1° amine condenses with an aldehyde to give an imine, and the imine is reduced catalytically to the 2° amine. No over-alkylation is possible because the carbonyl supplies exactly one carbon fragment.

Step 1. $R-NH_2 + R_2-CHO \longrightarrow R-N=CH-R_2 + H_2O$ (imine; R_2 is a generic second alkyl group).

Step 2. $R-N=CH-R_2 + H_2 \xrightarrow{Pt} R-NH-CH_2-R_2$ (2° amine).

Step 3. (i) gives a mixture: R_2NH, R_3N, R_4N^+ side products.

Step 4. (ii) gives $R-CH_2-NH_2$, a 1° amine (not 2°).

Step 5. (iv) Gabriel gives only 1° amines (single alkylation on phthalimide).

Final Answer: Reductive amination of a 1° amine with an aldehyde; option **(iii)**.

☞ **Why (i) fails**

$NH_3 + R-X$ always over-alkylates because each new amine product is more nucleophilic than ammonia itself. To stop at 2° cleanly you need a controlled C–N bond-forming step like reductive amination.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Stop-at-secondary angle. The constraint is to make exactly a 2° amine, not a mixture. Direct alkylation with NH_3 overshoots into tertiary and quaternary ammonium salts, and Gabriel is locked at primary by design. The cyanide-plus-hydrogenation route gives a 1° amine ($R-CH_2-NH_2$), not secondary. That leaves reductive amination: a 1° amine and an aldehyde condense to a single imine, hydrogenation reduces it cleanly to the secondary amine, and the stoichiometry naturally caps the process at one $N-C$ bond addition. That single-step, single-product profile is exactly what "most appropriate" demands.

Final Answer: Option **(iii)**.

Q 9.10 **The best reagent for converting 2-phenylpropanamide into 2-phenylpropan-**

amine is _____.
(i) excess H_2 (ii) Br_2 in aqueous NaOH
(iii) iodine in the presence of red phosphorus (iv) $LiAlH_4$ in ether

SOLUTION

Correct option: (iv) $LiAlH_4$ in ether.
Concept used. Reduction of an amide $R-CONH_2$ with $LiAlH_4$ converts the carbonyl $C=O$ into CH_2 and preserves the $C-N$ bond *without* loss of carbon. So the carbon count is unchanged — 2-phenylpropanamide ($C_6H_5-CH(CH_3)-CONH_2$, 9 C) $\rightarrow$ 2-phenylpropanamine ($C_6H_5-CH(CH_3)-CH_2-NH_2$, 9 C).

Step 1. $R-CONH_2 + 4\,[H] \xrightarrow{LiAlH_4} R-CH_2-NH_2 + H_2O$.

Step 2. (ii) $Br_2/NaOH$ is Hoffmann bromamide $\Rightarrow$ would lose one C, giving 1-phenylethanamine (asked in Q11).

Step 3. (i) Plain H_2 does not reduce amides; (iii) is a P/I combination for halide reduction, not amides.

Final Answer: $LiAlH_4$/ether; option **(iv)**.

☞ **Same-C vs. −1-C**
Amide $\rightarrow$ amine with $LiAlH_4$: same carbon count. Amide $\rightarrow$ amine with Hoffmann $Br_2/NaOH$: one carbon lost as carbonate.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Keep-the-carbon angle. The two products in Q10 and Q11 are constitutional cousins of the same amide, differing only by one carbon. To go from $R-CONH_2$ to $R-CH_2-NH_2$ (one more carbon than the Hoffmann product), the $C=O$ has to be reduced all the way to CH_2 while preserving the $C-N$ bond — exactly what lithium aluminium hydride does to amides. So $LiAlH_4$ is the reagent that converts 2-phenylpropanamide into 2-phenylpropanamine without losing a carbon.

Final Answer: Option **(iv)**.

Q 9.11 **The best reagent for converting 2-phenylpropanamide into 1-phenylethanamine is _____.**
(i) excess H_2/Pt (ii) $NaOH/Br_2$
(iii) $NaBH_4$/methanol (iv) $LiAlH_4$/ether

SOLUTION

Correct option: (ii) $NaOH/Br_2$ (Hoffmann bromamide degradation).
Concept used. **Hoffmann bromamide** converts $R-CONH_2$ into $R-NH_2$, dropping the carbonyl carbon as Na_2CO_3. Apply to 2-phenylpropanamide $C_6H_5-CH(CH_3)-CONH_2$ (9 C) and the product is $C_6H_5-CH(CH_3)-NH_2$ (8 C) = 1-phenylethanamine.

Step 1. $R-CONH_2 + Br_2 + 4\,NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O$.

Step 2. Mechanism: N-bromination $\rightarrow$ deprotonation $\rightarrow$ α-elimination to isocyanate $R-N=C=O$ $\rightarrow$ hydrolysis to $R-NH_2$.

Step 3. (iv) $LiAlH_4$ gives 2-phenylpropanamine (same C count), not 1-phenylethanamine.

> **Final Answer:** Hoffmann bromamide with $NaOH/Br_2$; option **(ii)**.

☞ **Read the carbon count!**
1-phenylethanamine has 8 C, 2-phenylpropanamide has 9 C; the route must lose one C $\Rightarrow$ Hoffmann bromamide.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Lose-one-carbon angle. The product 1-phenylethanamine $C_6H_5-CH(CH_3)-NH_2$ has one fewer carbon than the starting 2-phenylpropanamide $C_6H_5-CH(CH_3)-CONH_2$, so the route must shed a carbon. Hoffmann bromamide degradation is the textbook "one carbon shorter" reaction — treatment with $Br_2/NaOH$ converts the primary amide to the corresponding amine while expelling the carbonyl carbon as carbonate. So $Br_2/NaOH$ is the right pick.

> **Final Answer:** Option **(ii)**.

Q 9.12 **Hoffmann Bromamide Degradation reaction is shown by _____.**
(i) $ArNH_2$ **(ii)** $ArCONH_2$ **(iii)** $ArNO_2$ **(iv)** $ArCH_2NH_2$

SOLUTION

Correct option: (ii) $ArCONH_2$, a primary aryl amide.
Concept used. The Hoffmann bromamide rearrangement requires a substrate with the $-CONH_2$ functional group — i.e. a primary amide. The two N–H bonds are essential (one is brominated, the other is deprotonated). Amines, nitro arenes and $-CH_2NH_2$ are not amides and do not undergo this rearrangement.

Step 1. Generic Hoffmann:
$\mathrm{R{-}CONH_2 + Br_2 + 4\,NaOH \longrightarrow R{-}NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O}$.

Step 2. Step 1: N-bromination of $-\mathrm{CONH_2}$ gives $-\mathrm{CONHBr}$.

Step 3. Step 2: deprotonation, α-elimination to acyl nitrene; alkyl/aryl group migrates from C to N.

Step 4. Step 3: the isocyanate $\mathrm{R{-}N{=}C{=}O}$ hydrolyses to $\mathrm{R{-}NH_2 + CO_2}$.

Step 5. N-substituted amides ($\mathrm{R{-}CONH{-}R_2}$) lack the second N–H and do not undergo Hoffmann.

Final Answer: Only primary amide $\mathrm{ArCONH_2}$ undergoes Hoffmann; option **(ii)**.

✗ Don't confuse amide with amine

The N atom is the same letter but the functional group is different. "-$\mathrm{CONH_2}$" (amide) reacts; "-$\mathrm{NH_2}$" (amine) does not.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Functional-group-first angle. Hoffmann bromamide is named after its substrate — the primary *bromamide*, i.e. an $\mathrm{R{-}CONH_2}$ amide that has had one $\mathrm{N{-}H}$ replaced by $\mathrm{N{-}Br}$. The rearrangement only fires on a primary amide that carries two $\mathrm{N{-}H}$ bonds, one of which is brominated and the other of which is deprotonated to drive the migration. Aryl amines and aryl nitro compounds lack the carbonyl, while $\mathrm{ArCH_2NH_2}$ is again an amine, not an amide. Only $\mathrm{ArCONH_2}$ qualifies.

Final Answer: Option **(ii)**.

Q 9.13 **The correct increasing order of basic strength for the following compounds is _____.**

(I) Aniline (II) p-nitroaniline (III) p-toluidine

(i) II < III < I (ii) III < I < II (iii) III < II < I (iv) II < I < III

SOLUTION

Correct option: (iv) II < I < III.

Concept used. Aromatic amine basicity is governed by how much electron density sits on N. **Electron-donating** para substituents ($-\mathrm{CH_3}$, $+I$, $+H$) push density onto N ⇒

stronger base. **Electron-withdrawing** groups ($-NO_2$, $-M$, $-I$) pull density out of N via the ring $\Rightarrow$ weaker base.

Step 1. *p*-nitroaniline (II): $-NO_2$ strongly withdraws by $-M/-I$ $\Rightarrow$ weakest.

Step 2. Aniline (I): only the ring delocalisation drains N $\Rightarrow$ intermediate.

Step 3. *p*-toluidine (III): $-CH_3$ donates by $+I$/hyperconjugation $\Rightarrow$ strongest.

> **Final Answer:** II < I < III; option **(iv)**.

☞ pK_b **benchmarks**

p-toluidine ~ 8.9; aniline ~ 9.4; *p*-nitroaniline ~ 13.0. Smaller pK_b $\Rightarrow$ stronger base.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Substituent-effect angle. For substituted anilines, basicity tracks the electron density on the N lone pair, which in turn tracks what the para substituent does to the ring. An electron-donating group like *para*-methyl pushes density into the ring through $+I$ (and weak hyperconjugation) and pulls it back out toward N, boosting basicity. An electron-withdrawing group like *para*-nitro does the opposite: it has $-M$ and $-I$, so it siphons density off N through resonance structures that place a positive charge directly on the amino group ($-N^+=C$), crashing the basicity by several pK_b units. Aniline itself sits in the middle as the unsubstituted benchmark. So the basicity order, weakest $\rightarrow$ strongest, is $p-NO_2-C_6H_4-NH_2 < C_6H_5-NH_2 < p-CH_3-C_6H_4-NH_2$.

> **Final Answer:** II < I < III; option **(iv)**.

Q 9.14 **Methylamine reacts with HNO_2 to form _____.**

(i) $CH_3-O-N=O$ **(ii)** CH_3-O-CH_3 **(iii)** CH_3OH **(iv)** CH_3CHO

SOLUTION

Correct option: (iii) CH_3OH (methanol).

Concept used. 1° aliphatic amines and HNO_2 give an unstable aliphatic diazonium ion that fragments at once to N_2 plus a carbocation; water traps the cation to give an alcohol. For methylamine the cation is CH_3^+ and the isolated organic product is methanol.

Step 1. $CH_3NH_2 + HNO_2 \longrightarrow CH_3-N_2^+ + 2\,H_2O$.

Step 2. $CH_3-N_2^+ \longrightarrow CH_3^+ + N_2\uparrow$ (the gas).

Step 3. $CH_3^+ + H_2O \longrightarrow CH_3OH + H^+$.

Final Answer: Methanol, CH_3OH; option **(iii)**.

☞ **Paired with Q15**

The brisk gas in Q15 is N_2; the organic product here is the alcohol CH_3OH. Both come from the same diazonium decomposition.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Diazonium-then-water angle. 1° aliphatic amines plus HNO_2 go through three quick steps: (1) protonation and nitrosation of N to give an unstable diazonium ion $R{-}N{\equiv}N^+$, (2) spontaneous loss of N_2 (a fantastic leaving group) to give a carbocation, (3) capture of the cation by water to give the alcohol. For methylamine the cation is methyl, and the trapped product is methanol. Brisk frothing of N_2 is the gas, the alcohol is the liquid.

Final Answer: Option **(iii)** CH_3OH.

Q 9.15 **The gas evolved when methylamine reacts with nitrous acid is _____.**

(i) NH_3 **(ii)** N_2 **(iii)** H_2 **(iv)** C_2H_6

SOLUTION

Correct option: (ii) N_2.

Concept used. Primary aliphatic amines react with HNO_2 (generated *in situ* from $NaNO_2 + HCl$) to give an unstable **aliphatic diazonium** salt $R{-}N_2^+\,X^-$. Unlike aryl diazonium salts (which are stable at $0 - 5\,^\circ C$), the aliphatic one decomposes *at once* to release N_2 and a carbocation that is trapped by water to give the corresponding alcohol.

Step 1. $CH_3NH_2 + HNO_2 \longrightarrow CH_3{-}N_2^+ + 2\,H_2O$ (diazotisation).

Step 2. Spontaneous: $CH_3{-}N_2^+ \longrightarrow CH_3^+ + N_2\uparrow$ (the gas evolved).

Step 3. $CH_3^+ + H_2O \longrightarrow CH_3OH + H^+$ (final product methanol).

Final Answer: Brisk evolution of N_2 gas confirms a 1° aliphatic amine; option **(ii)**.

☞ **Lab test for 1° aliphatic amine**

A frothy, brisk release of N_2 at room temperature on adding $NaNO_2/HCl$ confirms 1°

aliphatic amine. 2° gives a yellow oily N-nitrosamine; 3° gives only a soluble salt.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Mechanism-shortcut angle. The diazonium cation $R{-}N{\equiv}N^+$ is intrinsically unstable when R is an aliphatic group, because the leaving fragment N_2 is one of the best leaving groups known and there is no aromatic ring to delocalise the carbocation that forms. The instant the methyl diazonium $CH_3{-}N_2^+$ is generated, it spits out N_2 quantitatively and gives a methyl cation that water grabs to give methanol. The brisk frothing of N_2 at room temperature is the classroom test for a 1° aliphatic amine.

Final Answer: N_2 gas evolves; option **(ii)**.

Q 9.16 **In the nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3, the species which initiates the reaction is _____.**

(i) NO_2 **(ii)** NO^+ **(iii)** NO_2^+ **(iv)** NO_2^-

SOLUTION

Correct option: (iii) the nitronium ion NO_2^+.

Concept used. In the mixed-acid nitration of arenes, H_2SO_4 protonates HNO_3 and water leaves to generate the **nitronium ion** NO_2^+. NO_2^+ is the actual electrophile that attacks the benzene ring.

Step 1. $HNO_3 + H_2SO_4 \longrightarrow H_2NO_3^+ + HSO_4^-$.

Step 2. $H_2NO_3^+ \longrightarrow NO_2^+ + H_2O$.

Step 3. $C_6H_6 + NO_2^+ \longrightarrow [\text{arenium}] \longrightarrow C_6H_5{-}NO_2 + H^+$.

Step 4. NO, NO^+ and NO_2^- never enter the mechanism in this medium.

Final Answer: NO_2^+; option **(iii)**.

☞ **Linked to amine chemistry**

Aniline nitration uses the same NO_2^+, but H_2SO_4 first protonates $-NH_2$ to the m-directing $-NH_3^+$; that is why we acetylate aniline before nitration.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Generate-the-electrophile angle. The mixed-acid nitrating reagent is not nitric acid directly; the sulphuric acid (the stronger acid) protonates nitric acid and ejects water to give the linear nitronium ion $O{=}N^{+}{=}O$. That cation has a genuine vacant orbital on N and a $+1$ formal charge, making it electrophilic enough to attack benzene's π cloud. The neutral NO_2 radical and the anion NO_2^{-} are not electrophiles, while NO^{+} is the diazotisation electrophile (different reaction).

Final Answer: NO_2^{+}.

Q 9.17 **Reduction of aromatic nitro compounds using Fe and HCl gives _____.**
(i) aromatic oxime (ii) aromatic hydrocarbon
(iii) aromatic primary amine (iv) aromatic amide

SOLUTION

Correct option: (iii) aromatic primary amine.
Concept used. Fe/HCl is a dissolving-metal acidic reductant that converts $Ar{-}NO_2$ all the way to the 1° aryl amine $Ar{-}NH_2$. The same outcome as Sn/HCl or Zn/HCl, but cheaper $\Rightarrow$ used industrially.

Step 1. Overall: $C_6H_5NO_2 + 3\,Fe + 7\,HCl \longrightarrow C_6H_5NH_3^{+}\,Cl^{-} + 3\,FeCl_2 + 2\,H_2O$, then base gives $C_6H_5NH_2$.

Step 2. $FeCl_2$ hydrolyses ($FeCl_2 + 2\,H_2O \longrightarrow Fe(OH)_2 + 2\,HCl$), regenerating HCl $\Rightarrow$ only catalytic acid is needed.

Final Answer: 1° aryl amine; option **(iii)**.

♥ Plant scale

Fe/HCl is the workhorse on the aniline plant scale because the HCl is effectively catalytic — the $FeCl_2$ by-product hydrolyses to give back HCl, so only a small charge of acid is needed (linked to Q72 reasoning).

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Reagent-recall angle. The trio Sn/HCl, Fe/HCl and Zn/HCl all do the same job on aryl nitro compounds — they deliver electrons in an acidic medium and walk the nitro group through nitroso and hydroxylamine to a clean primary aryl amine. Fe/HCl is the

cheapest variant and the only one used at industrial scale (e.g. the Bechamp process for aniline). The other options (oxime, hydrocarbon, amide) require entirely different reagents.

Final Answer: Aromatic primary amine; option **(iii)**.

Q 9.18 **The most reactive amine towards dilute hydrochloric acid is _____.**
(i) CH_3-NH_2 **(ii)** $(CH_3)_2NH$ **(dimethylamine)**
(iii) $(CH_3)_3N$ **(trimethylamine)** **(iv) Aniline** ($C_6H_5-NH_2$)

SOLUTION

Correct option: (ii) dimethylamine, $(CH_3)_2NH$.
Concept used. Reactivity towards dilute HCl tracks aqueous basicity. The well-known order is $2^\circ > 1^\circ \approx 3^\circ > NH_3 \gg$ aryl amines. Dimethylamine $(CH_3)_2NH$ sits at the top of that ladder in the methyl series.

Step 1. $(CH_3)_2NH$: two $+I$ methyls + one $N-H$ for solvating $H_2N(CH_3)_2^+ \Rightarrow$ strongest.

Step 2. CH_3NH_2: one $+I$ methyl + two $N-H \Rightarrow$ moderate.

Step 3. $(CH_3)_3N$: three $+I$ methyls but zero $N-H \Rightarrow$ poor cation solvation $\Rightarrow$ weaker in water.

Step 4. $C_6H_5NH_2$: lone pair delocalised into ring $\Rightarrow$ weakest.

Final Answer: $(CH_3)_2NH$ is most reactive towards dilute HCl; option **(ii)**.

☞ **Three forces in water**
Aqueous basicity is set by three competing factors: $+I$ donation (favours 3°), hydration of $R-NH_3^+$ (favours 1°), and steric crowding around N (penalises 3°). The compromise winner is the 2° amine.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Compromise-wins angle. Three effects compete when an amine encounters water. $+I$ donation by alkyl groups grows from $1^\circ \to 3^\circ$. Hydration of the ammonium cation $R_nNH_{(4-n)}^+$ improves as the number of $N-H$ bonds that can hydrogen-bond to water grows — so it falls from 1° to 3°. Steric crowding around N also grows from 1° to 3°, blocking protonation. Dimethylamine maximises the sum: two methyls give plenty of $+I$, one residual $N-H$ still solvates the cation, and steric crowding is moderate. Trimethylamine has more $+I$ but loses to poor cation solvation; methylamine has more

solvation but loses to weaker $+I$; aniline loses on every count because of ring conjugation.

> **Final Answer:** Option **(ii)** dimethylamine.

Q 9.19 **Acid anhydrides on reaction with primary amines give _____.**
(i) amide (ii) imide (iii) secondary amine (iv) imine

SOLUTION

Correct option: (i) an amide.
Concept used. Acylation of amines: the amine nitrogen attacks a carbonyl carbon of the acid anhydride, displacing carboxylate, to give an N-acyl amide. With a 1° amine and acetic anhydride, the product is an N-substituted acetamide.

Step 1. $\mathrm{R{-}NH_2} + (\mathrm{R_2{-}CO})_2\mathrm{O} \longrightarrow \mathrm{R{-}NH{-}CO{-}R_2} + \mathrm{R_2{-}COOH}$.

Step 2. Example: $\mathrm{C_6H_5{-}NH_2} + (\mathrm{CH_3CO})_2\mathrm{O} \longrightarrow \mathrm{C_6H_5{-}NH{-}COCH_3} + \mathrm{CH_3COOH}$ (acetanilide, the textbook example).

Step 3. Pyridine is often added to mop up the carboxylic acid that is co-produced.

> **Final Answer:** Amide ($\mathrm{R{-}NH{-}CO{-}R_2}$); option **(i)**.

☞ **Why one acylation only**
The freshly formed amide nitrogen is much less nucleophilic than the starting amine (carbonyl resonance drains N), so a second acylation is slow $\Rightarrow$ acylation is mono-substituting (unlike alkylation).

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Acyl-transfer angle. An acid anhydride has two acyl groups linked through a shared oxygen and is a good acyl-donor electrophile. A primary amine attacks one of the two carbonyl carbons with its nitrogen lone pair, the tetrahedral intermediate collapses with loss of carboxylate, and the product is the N-acyl amide $\mathrm{R{-}NH{-}CO{-}R_2}$ plus a carboxylic acid byproduct. The nitrogen now bears an acyl group rather than an extra alkyl group, so the new C–N bond defines an amide, not a secondary amine.

> **Final Answer:** An amide; option **(i)**.

Q 9.20 **The reaction (with Cu metal in HCl)**

$$\mathrm{Ar{-}N_2^+\,Cl^- + Cu \longrightarrow Ar{-}Cl + N_2 + CuCl}$$

is named as _____.
(i) Sandmeyer reaction (ii) Gatterman reaction
(iii) Claisen reaction (iv) Carbylamine reaction

SOLUTION

Correct option: (ii) Gatterman reaction.
Concept used. Two closely related transformations convert an aryl diazonium chloride into an aryl halide. **Sandmeyer** uses cuprous halide CuX in HX; **Gatterman** uses freshly precipitated *copper powder* in HX. The question shows plain Cu metal (not CuCl) above the arrow and emits CuCl as a product — the textbook signature of the Gatterman variant.

Step 1. Sandmeyer (with cuprous chloride in HCl):

$$\mathrm{ArN_2^+\,Cl^- + CuCl \longrightarrow Ar{-}Cl + N_2 + CuCl}$$

(Cu(I) shuttles an electron back and forth.)

Step 2. Gatterman (with Cu metal in HCl; CuCl is generated in situ):

$$\mathrm{ArN_2^+\,Cl^- + Cu \longrightarrow Ar{-}Cl + N_2 + CuCl}$$

Step 3. The equation in the question matches the Gatterman pattern exactly.

Final Answer: Gatterman reaction; option **(ii)**.

☞ **Sandmeyer vs. Gatterman in one line**
Reagent on top of the arrow = **CuX** ⇒ Sandmeyer; reagent = **Cu** metal ⇒ Gatterman.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Read-the-arrow angle. The reagent over the arrow is plain elemental copper in HCl, not the cuprous chloride that the Sandmeyer reaction calls for. That single difference is decisive — Gatterman's modification was designed to dodge the awkward preparation of CuCl by using freshly reduced copper powder in concentrated HCl. The cuprous chloride that turns up on the right-hand side of the given equation is generated in situ from that copper, confirming the route. Both routes serve the same synthetic end (replacing $\mathrm{N_2^+}$ by Cl on the ring), but the question's stoichiometry is uniquely Gatterman.

Final Answer: Gatterman reaction; option **(ii)**.

Q 9.21 **Best method for preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is _____.**
(i) Hoffmann Bromamide reaction (ii) Gabriel phthalimide synthesis
(iii) Sandmeyer reaction (iv) Reaction with NH_3

SOLUTION

Correct option: (ii) Gabriel phthalimide synthesis.
Concept used. The question demands two things: (a) start from **alkyl halide**, (b) keep the same carbon count. Gabriel synthesis substitutes N from phthalimide onto $R-X$ via S_N2 and then hydrolyses to $R-NH_2$ — the carbon skeleton from $R-X$ is conserved exactly.

Step 1. Reject (i) Hoffmann: starts from *amide* ($R-CONH_2$), not $R-X$, and *loses* one C.

Step 2. Reject (iii) Sandmeyer: starts from aryl *diazonium*, not alkyl halide.

Step 3. (iv) $NH_3 + R-X$ works on alkyl halides but over-alkylates, giving a mix — not the "best" method.

Step 4. (ii) Gabriel: alkyl halide $\rightarrow$ pure 1° amine, same C count, no over-alkylation.

Final Answer: Gabriel phthalimide synthesis; option **(ii)**.

✗ Gabriel fails for $Ar-X$!
Aryl halides don't do S_N2, so Gabriel works only for 1° and 2° *alkyl* halides — never for aniline-type targets.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Constraints-first angle. Treat the question as a two-filter sieve. *Filter 1* — the substrate is an alkyl halide $R-X$: that immediately disqualifies Sandmeyer, which begins from an aryl diazonium salt ArN_2^+ and never sees an alkyl halide. *Filter 2* — the carbon count must not change: that kicks out the Hoffmann bromamide route, which (a) starts from an amide rather than $R-X$ and (b) loses one carbon as Na_2CO_3 during the rearrangement.
That leaves NH_3-ammonolysis versus Gabriel synthesis. Plain ammonia attacks $R-X$ but the resulting amine is more nucleophilic than ammonia itself, so a second, third and

fourth alkylation give a mess of $1^\circ/2^\circ/3^\circ/4^\circ$ products that are tough to separate. Gabriel sidesteps this trap by using phthalimide nitrogen, which can be alkylated only once, then hydrolysing to release a pure 1° amine with the same carbon skeleton as the parent halide.

> **Final Answer:** Gabriel phthalimide synthesis; option **(ii)**.

Q 9.22 **Which of the following compounds will not undergo azo coupling reaction with benzene diazonium chloride?**
(i) Aniline (ii) Phenol (iii) Anisole (iv) Nitrobenzene

SOLUTION

Correct option: (iv) Nitrobenzene.
Concept used. **Azo coupling** is an electrophilic aromatic substitution in which ArN_2^+ is a *weak* electrophile and so needs a *strongly activated* aromatic ring (e.g. $-NH_2$, $-OH$, $-OR$). The ring in nitrobenzene is strongly **deactivated** by $-NO_2$ ($-M$, $-I$) and refuses coupling.

Step 1. Aniline ($-NH_2$): strong activator $\Rightarrow$ couples at p to give p-aminoazobenzene (yellow dye).

Step 2. Phenol ($-OH$): strong activator $\Rightarrow$ couples at p to give p-hydroxyazobenzene (orange dye).

Step 3. Anisole ($-OMe$): activator (lone pair on O donates) $\Rightarrow$ couples at p.

Step 4. Nitrobenzene ($-NO_2$): strongly deactivated $\Rightarrow$ no coupling.

> **Final Answer:** Nitrobenzene fails to couple; option **(iv)**.

☞ **Why ArN_2^+ is a weak electrophile**
$Ar-N\equiv N^+$ has the positive charge delocalised onto both nitrogens *and* the ring, so it is a mild electrophile. Only π-rich arenes are nucleophilic enough to couple with it.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Activator-vs-deactivator angle. Azo coupling needs an electron-rich ring because the aryl diazonium cation is a feeble electrophile. Aniline, phenol and anisole all carry strong o/p-directing activators ($-NH_2$, $-OH$, $-OMe$) whose lone pairs flood the para carbon with electron density, so each couples readily to give a coloured azo dye.

Nitrobenzene carries the strongly m-directing deactivator $-NO_2$, which makes the ring electron-poor at every coupling position. The encounter complex with ArN_2^+ is simply not stable enough to proceed, so nitrobenzene does not undergo azo coupling.

Final Answer: Option **(iv)**.

Q 9.23 **Which of the following compounds is the weakest Brönsted base?**
(i) Aniline ($C_6H_5NH_2$) **(ii) Cyclohexylamine** ($C_6H_{11}NH_2$)
(iii) Phenol (C_6H_5OH) **(iv) Cyclohexanol** ($C_6H_{11}OH$)

SOLUTION

Correct option: (iii) Phenol.
Concept used. Basicity depends on (a) which heteroatom holds the lone pair (N less electronegative than O $\Rightarrow$ N bases stronger), and (b) whether the lone pair is delocalised by an aromatic ring ($-M$ via resonance $\Rightarrow$ basicity drops sharply). Phenol combines both penalties — oxygen *and* ring conjugation — making it the weakest base in the set.

Step 1. Cyclohexylamine: aliphatic amine, no resonance, lone pair on N $\Rightarrow$ strongest ($pK_b \approx 3.4$).

Step 2. Aniline: aromatic amine, ring delocalisation drains lone pair $\Rightarrow$ weaker ($pK_b \approx 9.4$).

Step 3. Cyclohexanol: aliphatic alcohol, O holds lone pair tightly $\Rightarrow$ weaker base than amines.

Step 4. Phenol: $-OH$ on benzene $\Rightarrow$ lone pair delocalised into ring; phenol is actually a weak acid ($pK_a \approx 10$), *not* a base $\Rightarrow$ weakest base.

Final Answer: Phenol is the weakest Brönsted base; option **(iii)**.

☞ **Phenol is acidic, not basic**
Phenol's resonance makes the $-OH$ acidic (it loses H^+ to give a stabilised phenoxide). Acceptance of H^+ to give a phenyl oxonium $Ar-OH_2^+$ is extremely unfavourable, hence the weak basicity.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Heteroatom-and-ring angle. Run two filters across the four candidates. Filter one: nitrogen bases beat oxygen bases of the same skeleton, because nitrogen's lower electronegativity lets it donate its lone pair more readily. That immediately makes the

two alcohols weaker bases than the two amines. Filter two: aromatic substrates lose more basicity than aliphatic ones, because the ring lone-pair conjugation pulls density away from the heteroatom. So among the two alcohols, phenol is weaker than cyclohexanol — and phenol is actually acidic, not basic, on a $\mathrm{p}K_a$ scale. The weakest base of the four is therefore phenol.

> **Final Answer:** Option **(iii)**.

Q 9.24 **Among the following amines, the strongest Brönsted base is _____.**
(i) Aniline ($C_6H_5{-}NH_2$) (ii) NH_3
(iii) Pyrrole (aromatic 5-ring N–H) (iv) Pyrrolidine (saturated 5-ring N–H)

SOLUTION

Correct option: (iv) Pyrrolidine.
Concept used. Pyrrolidine is a saturated 2° aliphatic amine $\Rightarrow$ lone pair on N is fully sp^3 and available for protonation. Pyrrole is *aromatic*; its N lone pair sits in the aromatic π system and is not available for H^+ acceptance. Aniline and NH_3 are weaker than aliphatic amines.

Step 1. Pyrrolidine: $\mathrm{p}K_b \approx 2.9$ — a strong base (like piperidine).

Step 2. NH_3: $\mathrm{p}K_b \approx 4.7$.

Step 3. Aniline: $\mathrm{p}K_b \approx 9.4$ (ring delocalisation drains lone pair).

Step 4. Pyrrole: $\mathrm{p}K_b \gg 14$; using its N lone pair for H^+ would destroy aromaticity $\Rightarrow$ extremely weak base.

> **Final Answer:** Pyrrolidine, option **(iv)**, is by far the strongest base in the set.

☞ Pyrrole's lone pair lives in π

In pyrrole the N contributes two electrons to the 6π aromatic system. Protonating N would remove those two electrons and break aromaticity — huge energy cost, hence the very weak basicity. Pyridine's N lone pair sits in an sp^2 orbital outside the ring, so it *is* basic.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Where-is-the-lone-pair angle. The cleanest discriminator in this question is whether the nitrogen lone pair sits in the aromatic π system or in a localised sp^3 orbital. Pyrrole's N donates its lone pair into the ring to complete the 6π aromatic count, so protonation

of N would destroy aromaticity — a steep energy penalty that suppresses its basicity to almost zero. Aniline's lone pair is partially delocalised into the benzene ring, which weakens but does not eliminate basicity. Ammonia is the unsubstituted benchmark. Pyrrolidine is the only fully saturated, 2° aliphatic amine in the set — its lone pair is fully localised on sp^3 nitrogen and reinforced by two $+I$ alkyl groups, so it is the strongest base.

Final Answer: Option **(iv)** pyrrolidine.

Q 9.25 **The correct decreasing order of basic strength of the following species is _____.**

H_2O, NH_3, OH^-, NH_2^-

(i) $NH_2^- > OH^- > NH_3 > H_2O$ **(ii)** $OH^- > NH_2^- > H_2O > NH_3$

(iii) $NH_3 > H_2O > NH_2^- > OH^-$ **(iv)** $H_2O > NH_3 > OH^- > NH_2^-$

SOLUTION

Correct option: (i) $NH_2^- > OH^- > NH_3 > H_2O$.

Concept used. Two trends operate together: (a) anionic forms (NH_2^-, OH^-) are far stronger bases than the neutral parents (NH_3, H_2O), because the lone pair is unshared; (b) for the same charge type, nitrogen bases beat oxygen bases (N less electronegative $\Rightarrow$ donates lone pair more readily).

Step 1. NH_2^-: anion on N $\Rightarrow$ strongest base.

Step 2. OH^-: anion on O $\Rightarrow$ strong, but less so than NH_2^- (O holds lone pair more tightly).

Step 3. NH_3: neutral N $\Rightarrow$ moderate base ($pK_b \approx 4.7$).

Step 4. H_2O: neutral O $\Rightarrow$ weak base.

Final Answer: $NH_2^- > OH^- > NH_3 > H_2O$; option **(i)**.

☞ **Conjugate-acid check**

NH_2^-'s conjugate acid is NH_3 ($pK_a \approx 36$); OH^-'s conjugate acid is H_2O ($pK_a \approx 16$); the gap of ~ 20 orders confirms NH_2^- is the stronger base.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Charge-then-electronegativity angle. Two independent factors decide the ordering. The first is overall charge: a formal negative on the heteroatom (as in NH_2^- or OH^-) makes the lone pair vastly more eager to grab H^+ than the neutral parents NH_3 or H_2O. The second is which heteroatom carries the charge: for both the charged and the neutral pair, the nitrogen species is a stronger base because nitrogen is less electronegative and holds its lone pair more loosely. Stacking the two filters gives $NH_2^- > OH^- > NH_3 > H_2O$.

> **Final Answer:** Option **(i)**.

Q 9.26 **Which of the following should be most volatile?**

(I) $CH_3CH_2CH_2NH_2$ **(II)** $(CH_3)_3N$

(III) $CH_3CH_2{-}NH{-}CH_3$ **(IV)** $CH_3CH_2CH_3$

Choose: (i) II (ii) IV (iii) I (iv) III

SOLUTION

Correct option: (ii) IV, propane.

Concept used. Volatility is the inverse of boiling point. Boiling point rises with the strength of *intermolecular* attractions — the dominant one here is **hydrogen bonding**, which requires $N{-}H$ or $O{-}H$. Propane has only weak London forces; trimethylamine has no $N{-}H$; methylethylamine has one $N{-}H$; n-propylamine has two $N{-}H$. So the BP ladder is propane < trimethylamine < methylethylamine < n-propylamine $\Rightarrow$ propane is the most volatile.

Step 1. Propane: BP $-42\,^\circ C$ (no H-bonding).

Step 2. Trimethylamine (3° amine): BP $+3\,^\circ C$ (no $N{-}H$).

Step 3. N-methylethylamine (2°): BP $\sim 37\,^\circ C$ (one $N{-}H$).

Step 4. n-Propylamine (1°): BP $48\,^\circ C$ (two $N{-}H$).

> **Final Answer:** Propane (IV) is the most volatile; option **(ii)**.

☞ **H-bonding rule of thumb**

Per $N{-}H$ added, the BP of a similar-MW amine rises by $\sim 20{-}25\,^\circ C$ because of the extra H-bond donor sites.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Count-the-NH angle. The four molecules have nearly the same molar mass, so dispersion forces are roughly equal. The volatility ordering then collapses to the number of $\mathrm{N-H}$ bonds available for intermolecular hydrogen bonding. Propane has none and only dispersion forces, so it has the lowest boiling point and the highest volatility. Trimethylamine has no $\mathrm{N-H}$ either, but its N lone pair can still accept hydrogen bonds from neighbours (slight increase). N-methylethylamine adds one $\mathrm{N-H}$ donor, n-propylamine adds two. So the volatility ordering is propane $>$ trimethylamine $>$ N-methylethylamine $>$ n-propylamine, and the most volatile is propane.

Final Answer: Option **(ii)** IV (propane).

Q 9.27 **Which of the following methods of preparation of amines will give same number of carbon atoms in the chain of amines as in the reactant?**
(i) Reaction of nitrile with $\mathrm{LiAlH_4}$.
(ii) Reaction of amide with $\mathrm{LiAlH_4}$ followed by treatment with water.
(iii) Heating alkyl halide with potassium salt of phthalimide followed by hydrolysis.
(iv) Treatment of amide with bromine in aqueous solution of sodium hydroxide.

SOLUTION

Correct option: (iii) Gabriel phthalimide synthesis.
Concept used. Audit each route for carbon-count change:

- (i) Nitrile reduction: $\mathrm{R-C{\equiv}N + 4\,[H] \longrightarrow R-CH_2-NH_2}$ — the nitrile C becomes the new $\mathrm{CH_2}$ in the amine. Carbon count *rises by 1* relative to the parent halide; relative to the nitrile, same. Depends on how you count "reactant".
- (ii) Amide reduction by $\mathrm{LiAlH_4}$: $\mathrm{R-CONH_2 \longrightarrow R-CH_2-NH_2}$ — same carbon count as the amide.
- (iii) Gabriel: $\mathrm{Phth-NK + R-X \longrightarrow R-NH_2}$ — same carbon count as the alkyl halide (the only new C comes from phthalimide, which is removed on hydrolysis).
- (iv) Hoffmann bromamide: $\mathrm{R-CONH_2 \longrightarrow R-NH_2}$ — carbon count *drops by 1*.

Step 1. NCERT key explicitly marks (iii) as the correct answer (Gabriel preserves the carbon count of the starting alkyl halide exactly).

Final Answer: Gabriel synthesis preserves the carbon count of the alkyl halide $\Rightarrow$ option **(iii)**.

☞ **Chain-length cheat sheet**

• *Same C as* R−X: Gabriel, ammonolysis, azide. • *Same C as amide*: $LiAlH_4$. • +1 *C*: nitrile route. • −1 *C*: Hoffmann bromamide.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Carbon-balance angle. The question asks which route maps the reactant carbon framework one-to-one onto the amine. Gabriel synthesis answers this cleanly when "reactant" is read as the alkyl halide R−X — the phthalimide nitrogen is grafted on during alkylation, then sliced off during hydrolysis, so the amine's carbon skeleton matches the halide's exactly. Hoffmann bromamide instead loses one carbon as carbonate; nitrile reduction gains one carbon from the nitrile C. Amide reduction also preserves the count but the NCERT key flags only the Gabriel route here.

Final Answer: Option **(iii)**.

II. Multiple Choice Questions (Type-II)

☞ **Note**

In this section two or more options may be correct.

Q 9.28 **Which of the following cannot be prepared by Sandmeyer's reaction?**
(i) Chlorobenzene (ii) Bromobenzene (iii) Iodobenzene (iv) Fluorobenzene

SOLUTION

Correct options: (iii) and (iv) — iodobenzene and fluorobenzene.
Concept used. Sandmeyer's reaction needs the cuprous halide CuX (X = Cl, Br) to deliver X to the aryl radical generated from ArN_2^+. Cuprous *iodide* is not required: I^- from KI reacts *directly* with the diazonium salt — so iodobenzene is made without Cu (not strictly "Sandmeyer"). Cuprous *fluoride* doesn't work either; aryl fluorides use the **Balz–Schiemann** route via $ArN_2^+ BF_4^-$.

Step 1. Cl, Br: classic Sandmeyer with CuCl/HCl or CuBr/HBr.

Step 2. I: needs only KI, no Cu; not a true Sandmeyer.

Step 3. F: Sandmeyer fails; use HBF_4 then heat (Balz–Schiemann).

Final Answer: Sandmeyer fails for Ar−I and Ar−F — options **(iii), (iv)**.

☞ Halide-by-halide reagent table

Ar−Cl: $CuCl/HCl$ (Sandmeyer). Ar−Br: $CuBr/HBr$ (Sandmeyer). Ar−I: just KI at room temperature, no copper. Ar−F: HBF_4 to make $ArN_2^+\,BF_4^-$, then dry heat (Balz–Schiemann).

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Halide-by-halide angle. Walk down the four answer choices and ask, for each, whether the textbook Sandmeyer recipe (cuprous halide in HX on ArN_2^+) actually applies. Chlorobenzene and bromobenzene fall straight into Sandmeyer's sweet spot — Cu(I) chloride and Cu(I) bromide are the classic salts that mediate $ArN_2^+ \longrightarrow Ar-Cl$ and $ArN_2^+ \longrightarrow Ar-Br$ via a single-electron-transfer mechanism.
Iodobenzene is the trap. It is made from ArN_2^+, but no copper is required: iodide is such a good nucleophile that a plain solution of KI at room temperature does the job, so the transformation is not Sandmeyer in the strict sense. Fluorobenzene is even further outside Sandmeyer's reach — cuprous fluoride is unstable, so the route used industrially is Balz–Schiemann: trap the diazonium as the tetrafluoroborate $ArN_2^+\,BF_4^-$ and heat the dry salt. Hence the two "not by Sandmeyer" aryl halides are iodide and fluoride.

Final Answer: Options **(iii)** and **(iv)**.

Q 9.29 **Reduction of nitrobenzene by which of the following reagents gives aniline?**
(i) Sn/HCl (ii) Fe/HCl (iii) H_2-Pd (iv) Sn/NH_4OH

SOLUTION

Correct options: (i), (ii) and (iii) — Sn/HCl, Fe/HCl, and H_2/Pd.
Concept used. Reducing $C_6H_5-NO_2$ to $C_6H_5-NH_2$ needs *acidic* dissolving-metal conditions (Sn/HCl, Fe/HCl, Zn/HCl) or catalytic hydrogenation (H_2/Pt, Pd, Ni). Under *basic/neutral* conditions (Sn/NH_4OH, $LiAlH_4$), reduction halts at intermediate species (azoxybenzene, azobenzene, hydrazobenzene), not aniline.

Step 1. $C_6H_5NO_2 + 3\,Sn + 7\,HCl \longrightarrow C_6H_5NH_3^+\,Cl^- + 3\,SnCl_2 + 2\,H_2O$, then base gives $C_6H_5NH_2$.

Step 2. Fe/HCl is industrial: cheap, $FeCl_2$ hydrolyses to regenerate HCl (catalytic acid).

Step 3. Catalytic hydrogenation over Pd: $C_6H_5NO_2 + 3\,H_2 \longrightarrow C_6H_5NH_2 + 2\,H_2O$.

Step 4. Sn/NH_4OH is basic $\Rightarrow$ stops at azoxy/azo stage, not aniline.

Final Answer: (i), (ii), (iii) all give aniline; (iv) does not.

♥ Industrial scale

Fe/HCl is the workhorse on plant scale because iron is cheap and the $FeCl_2$ by-product hydrolyses to regenerate HCl, making the acid effectively catalytic. Catalytic H_2/Pd is preferred when traces of metal contamination cannot be tolerated — e.g. when the aniline goes on to dye or pharmaceutical synthesis.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Acidic-vs-basic angle. The textbook rule is that nitrobenzene reduces cleanly to aniline only when the reducing system supplies *both* electrons and protons. The acidic dissolving-metal trio — Sn/HCl, Fe/HCl, Zn/HCl — meets both requirements: the metal donates electrons, the strong acid keeps the intermediates protonated and funnels them downhill all the way to $Ar-NH_2$. Catalytic hydrogen over Pd is the other approved route; the metal surface dissociates H_2 into atomic hydrogen that walks the nitro group through nitroso, hydroxylamine and finally amine.
Sn in NH_4OH flips this picture upside down. The medium is basic, so the protonation steps that drive the reduction past azoxy- and azo-benzene never happen. Reduction simply stalls at azoxy- or azo-benzene (coloured by-products), and aniline is not formed. That is the standard trick question on this topic.

Final Answer: (i), (ii), (iii) all give aniline; (iv) stops short.

Q 9.30 **Which of the following species are involved in the carbylamine test?**
(i) $R-NC$ **(ii)** $CHCl_3$ **(iii)** $COCl_2$ **(iv)** $NaNO_2 + HCl$

SOLUTION

Correct options: (i) and (ii) — $R-NC$ and $CHCl_3$.
Concept used. The **carbylamine test** for 1° amines uses $CHCl_3$ and alcoholic KOH. The dichlorocarbene CCl_2 generated *in situ* reacts with $R-NH_2$ to give the foul-smelling **alkyl isocyanide** (carbylamine) $R-NC$. Phosgene $COCl_2$ and $NaNO_2$/HCl are reagents of different reactions (Schotten-Baumann and diazotisation, respectively).

Step 1. $CHCl_3 + KOH \longrightarrow CCl_2 + KCl + H_2O$ (α-elimination).

Step 2. $R-NH_2 + CCl_2 + 2\,KOH \longrightarrow R-NC + 2\,KCl + 2\,H_2O$.

Step 3. $R-NC$ is the product whose obnoxious smell flags a 1° amine.

Final Answer: Species involved: $CHCl_3$ and $R-NC$; options **(i), (ii)**.

☞ Carbylamine specifics

Carbylamine test fires only on 1° amines (both aliphatic and aromatic). 2° and 3° amines do not have the two $N-H$ needed for the double dehydrohalogenation, so they give nothing.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Mechanism-checklist angle. List what enters and what leaves the carbylamine test. Inputs: a primary amine $R-NH_2$, chloroform $CHCl_3$, and alcoholic potassium hydroxide. Output: alkyl isocyanide $R-NC$ (the source of the obnoxious smell) plus KCl and water. Of the four candidate species in the question, two appear in the balanced reaction: chloroform on the reactant side, alkyl isocyanide on the product side. Phosgene and the diazotising mixture $NaNO_2/HCl$ are reagents for other named transformations (Schotten-Baumann, diazotisation) and never enter the carbylamine equation.

Final Answer: Options **(i)** and **(ii)**.

Q 9.31 **The reagents that can be used to convert benzene diazonium chloride to benzene are _____.**

(i) $SnCl_2/HCl$ **(ii)** CH_3CH_2OH **(iii)** H_3PO_2 **(iv)** $LiAlH_4$

SOLUTION

Correct options: (ii) and (iii) — ethanol and hypophosphorous acid.

Concept used. Replacing the $-N_2^+$ group of an aryl diazonium salt by an $-H$ atom (i.e. *deamination*) is done with mild reducing agents that supply $H^{\bullet}$ or H^-. The two NCERT-listed reagents are **ethanol** (CH_3CH_2OH, which is oxidised to acetaldehyde) and **hypophosphorous acid** (H_3PO_2).

Step 1. Ethanol: $C_6H_5-N_2^+\,Cl^- + CH_3CH_2OH \longrightarrow C_6H_6 + N_2 + HCl + CH_3CHO$.

Step 2. Hypophosphorous acid:
$C_6H_5-N_2^+\,Cl^- + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$.

Step 3. $SnCl_2/HCl$ reduces $Ar-N_2^+$ to $Ar-NH-NH_2$ (phenylhydrazine), not benzene. $LiAlH_4$ is not the textbook reagent for this replacement.

Final Answer: Use CH_3CH_2OH or H_3PO_2; options **(ii), (iii)**.

☞ **Two-step deamination**

This is how the NCERT removes an $-NH_2$ group: aniline $\rightarrow$ benzene by diazotisation followed by reduction with H_3PO_2 or ethanol. Crucial for synthesising 1,3,5-trisubstituted arenes via temporary $-NH_2$ blocking.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Replace-by-H angle. Removing the diazonium group as N_2 and dropping a hydrogen in its place requires a mild hydride or hydrogen-atom donor. The NCERT-approved reagents are ethanol and hypophosphorous acid: ethanol is oxidised to acetaldehyde while delivering $H^{\bullet}$ to the aryl radical, and H_3PO_2 is oxidised to H_3PO_3 while doing the same. $SnCl_2/HCl$ over-reduces the diazonium to a phenylhydrazine $Ar-NH-NH_2$ (Bechamp variant), and $LiAlH_4$ tends to give phenylhydrazine or hydrazo products rather than clean replacement by hydrogen. So the right pair is ethanol and hypophosphorous acid.

Final Answer: Options **(ii)** and **(iii)**.

Q 9.32 **The product of the following reaction is _____.**

$$\textbf{Acetanilide} + Br_2/CH_3COOH \longrightarrow ?$$

(i) p-bromoacetanilide (ii) o-bromoacetanilide
(iii) m-bromoacetanilide (iv) 2,4,6-tribromoacetanilide

SOLUTION

Correct options: (i) and (ii) — p-bromoacetanilide (major) and o-bromoacetanilide (minor).

Concept used. Acetanilide $C_6H_5-NHCOCH_3$ has the $-NHCOCH_3$ group, a mild activator (lone pair on N delocalised into both the carbonyl and the ring), and an o/p-director with a strong steric bias for p. Br_2/CH_3COOH at room temperature gives mono-bromination at the activated o/p positions; over-bromination (as in aqueous Br_2) does not occur in acetic acid solvent.

Step 1. $-NHCOCH_3$ activates the ring less strongly than $-NH_2$ does (amide resonance into $C=O$ steals some lone-pair density from the ring).

Step 2. Bromination occurs only once $\Rightarrow$ mono-substituted product.

Step 3. Para is preferred over ortho on steric grounds (the bulky $NHCOCH_3$ group blocks ortho approach).

Final Answer: Mainly p-bromoacetanilide with some o-bromoacetanilide; options **(i), (ii)**.

☞ **Why acetanilide doesn't tribrominate**

Br_2 in aqueous medium gives 2,4,6-tribromoaniline because $-NH_2$ is a much stronger activator. Acetylation of N tames the ring; mild Br_2 in acetic acid stops at the first Br.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Tamed-activator angle. Acetylation of aniline replaces a free amine $-NH_2$ (very strong activator) by an amide $-NHCOCH_3$ (mild activator), because amide resonance siphons some of the nitrogen lone pair into the $C{=}O$ rather than into the ring. Under those conditions a single electrophilic bromination at the activated o/p positions is the natural outcome. The para position dominates because the bulky $NHCOCH_3$ blocks ortho approach. Hence the products are p-bromoacetanilide (major) and o-bromoacetanilide (minor); the tribromo product does not form under these mild conditions.

Final Answer: Options **(i)** and **(ii)**.

Q 9.33 **Arenium ion involved in the bromination of aniline is _____.**

(i) Cyclohexadienyl-$NH_2{}^+$-H-Br at C-2 (o-attack arenium)

(ii) Cyclohexadienyl with NH_2, with $+$ at $C{-}5$ and H, Br at C-2 (o-attack second resonance form)

(iii) Para arenium: $=NH_2{}^+$ at C-1, H, Br at C-4

(iv) Ortho arenium: NH_2 at C-1, $+$ at C-3, H, Br at C-2

SOLUTION

Correct options: (i), (ii) and (iii) — all three are valid arenium-ion (Wheland) intermediates for the bromination of aniline.

Concept used. An **arenium ion** (Wheland complex) forms when the electrophile Br^+ adds to a ring carbon, generating a cyclohexadienyl cation. For an o/p-director like $-NH_2$, the $+$ charge can be delocalised onto the carbon bearing $-NH_2$ via a resonance structure of type $R_2C{=}NH_2{}^+$, giving an extra-stable iminium contributor at *ortho* and *para* positions only (not meta).

Step 1. Ortho attack: Br goes to C-2; the $+$ charge delocalises through three positions, one of which puts it on the N atom as $=NH_2{}^+$ at C-1 (structure (i)). Other resonance forms place $+$ on C-3 or C-5 (structure (ii)).

Step 2. Para attack: Br goes to C-4; the + charge delocalises and one resonance form again puts it on N as $=NH_2^+$ at C-1 (structure (iii)).

Step 3. Meta attack (option (iv)) does not enjoy the iminium stabilisation ⇒ not a favoured arenium and not the answer.

> **Final Answer:** Bromination via o- and p-arenium intermediates; options **(i), (ii), (iii)**.

☞ **Where the iminium contributor sits**

The extra-stable $R_2C{=}NH_2^+$ contributor appears only when the attacked position is o or p to $-NH_2$. That is why $-NH_2$ is an o/p-director.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Resonance-stabilisation angle. When Br^+ attacks aniline, the resulting Wheland intermediate has the positive charge spread across three ring carbons. For o- and p-attack, one of those carbons is the same carbon that holds the NH_2 group — meaning the nitrogen lone pair can hop in and form a genuine $C{=}N^+$ bond, producing an iminium resonance structure that drops the energy of the intermediate substantially. For m-attack, the positive carbons never line up with the NH_2-bearing carbon, so the iminium structure is not accessible and the arenium is much less stable. That is why all three arenium drawings labelled o and p are valid (they are merely different resonance contributors of the same intermediate) and the meta drawing is not.

> **Final Answer:** Options **(i)**, **(ii)** and **(iii)**.

Q 9.34 **Which of the following amines can be prepared by Gabriel synthesis?**
(i) Isobutyl amine (ii) 2-Phenylethylamine
(iii) N-methylbenzylamine (iv) Aniline

SOLUTION

Correct options: (i) and (ii) — isobutyl amine and 2-phenylethylamine.
Concept used. Gabriel synthesis works only when the alkyl halide can undergo S_N2 on the phthalimide anion. Two structural conditions: (a) the halide must be a 1° (or 2°) *alkyl* halide, and (b) the product must be a *primary* amine ($R{-}NH_2$). Aryl halides ($C_6H_5{-}X$) do not do S_N2 and 2° amines (like N-methylbenzylamine) cannot come from a single alkylation of phthalimide.

Step 1. (i) Isobutyl amine: from $(CH_3)_2CH-CH_2-Br$ (1° alkyl halide) $\Rightarrow$ Gabriel OK.

Step 2. (ii) 2-Phenylethylamine: from $C_6H_5CH_2CH_2-Br$ (1° benzylic-adjacent) $\Rightarrow$ Gabriel OK.

Step 3. (iii) N-methylbenzylamine is 2° ($C_6H_5CH_2-NH-CH_3$); Gabriel gives only 1° amines $\Rightarrow$ fails.

Step 4. (iv) Aniline would need C_6H_5-Br + phthalimide anion $\Rightarrow$ S_N2 on sp^2 carbon fails.

Final Answer: Only (i) and (ii) are accessible by Gabriel synthesis.

✗ Two Gabriel "no-go" patterns

(a) Any *aryl* amine: phenyl-X won't react. (b) Any $2^\circ/3^\circ$ amine: only one alkylation can occur on phthalimide-N.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Filter-the-targets angle. Gabriel synthesis succeeds only when two boxes are ticked simultaneously: the starting halide must be an alkyl halide that can undergo backside S_N2 on the phthalimide nitrogen, and the final amine must be primary (so that one alkylation is enough). Run each target through this two-step sieve.
Aniline (iv) needs C_6H_5-X; that is an aryl halide where the sp^2 carbon refuses S_N2, so Gabriel is dead on arrival. N-methylbenzylamine (iii) is a secondary amine $C_6H_5CH_2-NH-CH_3$; phthalimide nitrogen carries only one ionisable hydrogen, so it can only deliver one alkyl group and hence only primary amines. Isobutyl amine (i) traces back to isobutyl bromide $(CH_3)_2CH-CH_2-Br$ — a clean primary alkyl halide that does S_N2 smoothly. 2-Phenylethylamine (ii) traces back to $C_6H_5-CH_2-CH_2-Br$, also primary alkyl (benzylic-adjacent, not benzylic itself) — again Gabriel-friendly. Hence only the latter two work.

Final Answer: (i) and (ii) only.

Q 9.35 **Which of the following reactions are correct?**

(i) $(CH_3)_2CHCl + 2\,NH_3 \longrightarrow (CH_3)_2CH-NH_2 + NH_4Cl$

(ii) $(CH_3)_2CHCl + \text{aq}\cdot\ KOH \longrightarrow$ **propene** $(CH_3-CH=CH_2)$

(iii) Cyclohexyl chloride + alc. KOH → cyclohexene

(iv) $(CH_3)_2CH-NH_2 + HNO_2 \xrightarrow{0\,^\circ C} (CH_3)_2CH-OH$

SOLUTION

Correct options: (i) and (iii).

Concept used. Audit each equation against the standard reactivity rules:

- (i) Ammonolysis of 2° alkyl halide with NH_3 gives a 1° amine $\Rightarrow$ correct.
- (ii) Aqueous KOH on a 2° alkyl halide gives the alcohol (substitution), *not* the alkene. Alkene formation needs *alcoholic* KOH (E2).
- (iii) Cyclohexyl chloride + alc. KOH $\rightarrow$ cyclohexene via E2 $\Rightarrow$ correct.
- (iv) Isopropylamine $+HNO_2$ gives isopropanol *only at room temperature, not at* $0\,^\circ C$ *as written for aryl diazotisation*; the equation pattern is right (aliphatic diazonium $\rightarrow$ alcohol $+N_2$), but the temperature label of $0\,^\circ C$ is the giveaway for the aryl pattern. The NCERT key marks (iv) as incorrect because the equation includes the $0\,^\circ C$ condition that belongs to aryl diazotisation.

Step 1. (i): $(CH_3)_2CHCl + 2\,NH_3 \longrightarrow (CH_3)_2CHNH_2 + NH_4Cl$ — one mole of NH_3 is the nucleophile, the other neutralises HCl. Correct.

Step 2. (ii): aqueous KOH supplies OH^-, the strong nucleophile in a polar medium. Substitution to give 2-propanol dominates; elimination is minor. The equation as written (forming the alkene) is wrong.

Step 3. (iii): alcoholic KOH supplies OH^- in a less-solvating medium where the small base is forced to deprotonate β-H, giving cyclohexene by E2.

Step 4. (iv): isopropylamine (1° aliphatic) does give 2-propanol with HNO_2, but it does so *spontaneously at room temperature* — the $0\,^\circ C$ label is reserved for aryl amines.

Final Answer: Correct equations: **(i)** and **(iii)**.

☞ Aq. vs. alc. KOH

• *Aqueous* KOH on $R-X$: $S_N2 \rightarrow$ alcohol. • *Alcoholic* KOH on $R-X$: E2 $\rightarrow$ alkene. The solvent decides whether substitution or elimination dominates.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Equation-audit angle. Score each equation independently on whether reagent, solvent, temperature and product match. Equation (i) is the textbook ammonolysis of a secondary alkyl halide — a single S_N2 delivers isopropylamine and an NH_4Cl byproduct, all consistent. Equation (iii) is the textbook E2 elimination on cyclohexyl chloride with alcoholic KOH, giving cyclohexene. Equation (ii) mismatches solvent and product: aqueous KOH on a secondary alkyl halide gives the alcohol via S_N2, not the alkene that the equation shows. Equation (iv) has the right product (isopropanol from a primary

aliphatic amine with HNO_2) but the wrong temperature label of $0\,^\circ C$, which belongs to aryl diazotisation; aliphatic diazonium ions decompose at room temperature. So only (i) and (iii) are fully correct.

> **Final Answer:** Options **(i)** and **(iii)**.

Q 9.36 **Under which of the following reaction conditions, aniline gives p-nitro derivative as the major product?**
(i) Acetyl chloride/pyridine followed by reaction with conc. H_2SO_4 + conc. HNO_3.
(ii) Acetic anhydride/pyridine followed by conc. H_2SO_4 + conc. HNO_3.
(iii) Dil. HCl followed by reaction with conc. H_2SO_4 + conc. HNO_3.
(iv) Reaction with conc. HNO_3 + conc. H_2SO_4.

SOLUTION

Correct options: (i) and (ii) — acylation (either reagent) first, then nitration gives p-nitroaniline as the major product.
Concept used. Direct nitration of aniline gives mostly the m-isomer because H_2SO_4 protonates $-NH_2$ to the m-directing $-NH_3^+$. Acetylating the amine first (with CH_3COCl or $(CH_3CO)_2O$ in pyridine) converts $-NH_2$ to the much less basic $-NHCOCH_3$, which stays o/p-directing under the strong-acid nitration conditions and gives mainly p.

Step 1. (i) Acetyl chloride/pyridine on aniline $\rightarrow$ acetanilide. Nitration of acetanilide $\rightarrow$ p-nitroacetanilide (major). Hydrolysis (acid) gives p-nitroaniline.

Step 2. (ii) Acetic anhydride/pyridine $\rightarrow$ acetanilide; same outcome as (i).

Step 3. (iii) Dil. HCl protonates aniline to anilinium (m-directing) before nitration $\Rightarrow$ m-nitroaniline, not p.

Step 4. (iv) Direct nitration: same anilinium-induced m-directing $\Rightarrow$ m-nitroaniline mainly.

> **Final Answer:** Acylate N first (any acyl chloride or anhydride) then nitrate; options **(i), (ii)**.

☞ **Pyridine's role here**
Pyridine sops up the HCl or CH_3COOH that acylation produces, preventing protonation of the amine and keeping the acylation clean.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Protect-before-nitrate angle. Aniline cannot be nitrated cleanly without protection because the nitrating mixture itself protonates $-NH_2$ to $-NH_3^+$, which is strongly m-directing and also so deactivating that the ring is prone to oxidation. The fix is to convert $-NH_2$ into an electron-balanced amide $-NHCOCH_3$ before nitration. Acetic anhydride or acetyl chloride, both in pyridine, do exactly that, yielding acetanilide whose $-NHCOCH_3$ is mildly activating and o/p-directing with a strong para bias on steric grounds. Nitration of acetanilide therefore gives mostly the p-nitro product, and acid hydrolysis unmasks p-nitroaniline.

Final Answer: Options **(i)** and **(ii)**.

Q 9.37 Which of the following reactions belong to electrophilic aromatic substitution?

(i) Bromination of acetanilide (ii) Coupling reaction of aryldiazonium salts

(iii) Diazotisation of aniline (iv) Acylation of aniline

SOLUTION

Correct options: (i) and (ii) — bromination of acetanilide and azo coupling.

Concept used. **Electrophilic aromatic substitution (EAS)** replaces a ring H with an electrophile while retaining aromaticity. The two-step arenium-ion mechanism applies. Reactions at the *nitrogen* of an amine (diazotisation, acylation) are *not* EAS even though aromatic amines are involved.

Step 1. (i) Acetanilide + Br_2/CH_3COOH: Br^+ attacks the ring at $p \Rightarrow$ EAS.

Step 2. (ii) Coupling: ArN_2^+ is the *electrophile* attacking another activated aromatic ring (phenol, aniline) $\Rightarrow$ EAS.

Step 3. (iii) Diazotisation: reaction at $-NH_2$ (not on ring); NO^+ attacks N $\Rightarrow$ not EAS.

Step 4. (iv) Acylation of aniline: $(CH_3CO)_2O$ acylates N to give acetanilide $\Rightarrow$ not EAS.

Final Answer: (i) and (ii) are EAS; (iii), (iv) react at N, not the ring.

☞ Spot an EAS in one glance

If the product has a new bond on a *ring carbon* and the ring is still aromatic, you are looking at EAS. If the new bond is on a heteroatom (here, on N of $-NH_2$), it is not EAS even when an arene is in the structure.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Site-of-attack angle. Run a single test on every option: *does the electrophile bond to a ring carbon, with loss of the ring proton?* If yes, the reaction is electrophilic aromatic substitution; otherwise it is something else even if an arene is involved.
(i) Bromination of acetanilide — Br^+ generated from Br_2/CH_3COOH attacks the para carbon of the strongly activated ring; aromaticity is restored on loss of H^+. Classic EAS. (ii) Azo coupling — the aryl diazonium cation $ArN_2{}^+$ is itself a mild electrophile that attacks an electron-rich arene (phenol or aniline) at the para ring carbon, giving the azo dye and losing the para H^+. Also EAS. (iii) Diazotisation — NO^+ (from HNO_2/HCl) adds to the *nitrogen* lone pair of $ArNH_2$, never touching the ring carbons. (iv) Acylation of aniline — acetic anhydride acylates the *nitrogen* of $-NH_2$ to give acetanilide, again sparing the ring. So only the first two count.

Final Answer: (i) and (ii).

III. Short Answer Type

Q 9.38 What is the role of HNO_3 in the nitrating mixture used for nitration of benzene?

SOLUTION

Answer: HNO_3 acts as a **base** in the nitrating mixture: it accepts H^+ from H_2SO_4 and then loses water to generate the actual electrophile, the **nitronium ion** $NO_2{}^+$.
Concept used. Generating an electrophile strong enough to attack benzene requires the cooperation of two acids: H_2SO_4 is the stronger acid (proton donor) and HNO_3 is the weaker acid; in their mutual presence, HNO_3 behaves as a base.

Step 1. Step 1 (acid-base): $HNO_3 + H_2SO_4 \longrightarrow H_2NO_3{}^+ + HSO_4{}^-$.

Step 2. Step 2 (water loss): $H_2NO_3{}^+ \longrightarrow NO_2{}^+ + H_2O$.

Step 3. Step 3 (nitronium attack): $C_6H_6 + NO_2{}^+ \longrightarrow C_6H_5{-}NO_2 + H^+$.

Step 4. Overall: HNO_3 provides the nitrogen by being protonated to give nitronium.

Final Answer: HNO_3 acts as a base, supplying $NO_2{}^+$ (the nitronium electrophile) on protonation by H_2SO_4.

☞ **Base behaviour rule**

In any pair of acids, the weaker acid acts as the conjugate base. H_2SO_4 ($pK_a \approx -3$) is stronger than HNO_3 ($pK_a \approx -1.4$), so HNO_3 gets protonated.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Generate-the-electrophile angle. The whole point of the mixed-acid recipe is to take an unreactive aromatic ring and a mildly electrophilic HNO_3 and combine them into a genuinely electrophilic attack on the arene. To do that, the nitric acid has to give up its $-OH$ as water and leave a nitrogen bearing a vacant orbital. Sulphuric acid, being the stronger acid, protonates nitric acid; the protonated nitric acid then dehydrates to the linear $O{=}N^{+}{=}O$ ion. So HNO_3's role is twofold — it is the source of the NO_2 group and it temporarily becomes a base by accepting the sulphuric acid proton.

Final Answer: HNO_3 behaves as a base; the product $NO_2{}^{+}$ is the active electrophile.

Q 9.39 Why is the $-NH_2$ group of aniline acetylated before carrying out nitration?

SOLUTION

Answer: Acetylation converts the strongly activating but basic $-NH_2$ into the mildly activating, non-basic $-NHCOCH_3$. This prevents (a) protonation of $-NH_2$ by H_2SO_4 to the m-directing $-NH_3{}^{+}$, and (b) oxidation of aniline by HNO_3.

Concept used. Three problems arise if aniline is nitrated directly:

- H_2SO_4 protonates the basic $-NH_2$ to $-NH_3{}^{+}$, which is strongly m-directing $\Rightarrow$ mostly m-nitroaniline.
- HNO_3 is a strong oxidant; aniline is electron-rich $\Rightarrow$ partial oxidation gives tarry residues.
- Even if some unprotonated aniline reacts, over-nitration to 2,4,6- and beyond is possible.

Step 1. Acetylation:

$$C_6H_5{-}NH_2 + (CH_3CO)_2O \xrightarrow{\text{pyridine}} C_6H_5{-}NHCOCH_3 + CH_3COOH.$$

Step 2. Acetanilide's N lone pair is partly delocalised into the carbonyl $\Rightarrow$ N is much less basic ($pK_b \approx 13.6$), so H_2SO_4 cannot protonate it.

Step 3. $-NHCOCH_3$ is still a mild activator and o/p-director; nitration gives mainly p-nitroacetanilide.

Step 4. Acid hydrolysis:

$$\text{p-}NO_2{-}C_6H_4{-}NHCOCH_3 + H_3O^{+} \longrightarrow \text{p-}NO_2{-}C_6H_4{-}NH_2 + CH_3COOH.$$

Final Answer: Acetyl protection keeps N neutral, prevents oxidation, and steers nitration cleanly to the para position.

✗ The direct route is a trap

A common JEE-style trick: "how do you nitrate aniline to give p-nitroaniline?" The wrong answer is "mixed acid directly". Always acetylate first, nitrate, then hydrolyse.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Two-pronged angle. Direct nitration of aniline fails for two parallel reasons. The sulphuric acid in the nitrating mix protonates the basic $-NH_2$ to $-NH_3^+$, flipping the director from o/p (the free amine) to m (the ammonium). The nitric acid in the mix oxidises the very electron-rich ring, giving black tarry oxidation products. Acetylation in pyridine solves both problems at once. The amide $-NHCOCH_3$ is so non-basic that even H_2SO_4 cannot protonate it, so the o/p-directing character is preserved through the nitration. The amide is also a much weaker activator than the free amine, so the ring is no longer prone to oxidation. After nitration, acid hydrolysis of the acetamide gives back the free amine, unmasked at the right ring position.

Final Answer: Acetylation protects $-NH_2$ from protonation and oxidation, preserving o/p-directing nitration.

Q 9.40 **What is the product when $C_6H_5CH_2NH_2$ reacts with HNO_2?**

SOLUTION

Product: Benzyl alcohol, $C_6H_5CH_2OH$.

Concept used. Benzylamine is a 1° *aliphatic* amine (the $-NH_2$ sits on an sp^3 benzylic carbon, not on the ring), so it follows the aliphatic-amine + HNO_2 pattern: unstable diazonium $\Rightarrow$ N_2 escapes $\Rightarrow$ H_2O traps the carbocation $\Rightarrow$ alcohol.

Step 1. $C_6H_5CH_2NH_2 + HNO_2 \longrightarrow C_6H_5CH_2{-}N_2^+ + 2\,H_2O$.

Step 2. $C_6H_5CH_2{-}N_2^+ \longrightarrow C_6H_5CH_2^+ + N_2\uparrow$ (benzylic cation is resonance-stabilised, decomposition is fast).

Step 3. $C_6H_5CH_2^+ + H_2O \longrightarrow C_6H_5CH_2OH + H^+$.

Final Answer: Benzyl alcohol, $C_6H_5CH_2OH$, with brisk evolution of N_2.

☞ **Aryl vs. benzyl amine + HNO_2**

Aniline ($C_6H_5-NH_2$, aryl) at $0-5\,^\circ C$ gives a *stable* diazonium salt. Benzylamine ($C_6H_5-CH_2-NH_2$, aliphatic) goes straight to the alcohol — the N_2 is lost instantly.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Classify-first angle. Decide whether the amine is aromatic (lone pair attached directly to sp^2 ring carbon) or aliphatic (lone pair on an sp^3 carbon). Benzylamine has the $-CH_2-$ buffer between the ring and the nitrogen, so it is aliphatic. Aliphatic primary amines plus HNO_2 always collapse via an unstable diazonium to the corresponding alcohol plus N_2 gas, so $C_6H_5CH_2NH_2$ gives $C_6H_5CH_2OH$.

> **Final Answer:** Benzyl alcohol $C_6H_5CH_2OH$ with N_2 release.

Q 9.41 What is the best reagent to convert nitrile to primary amine?

SOLUTION

Answer: Lithium aluminium hydride, $LiAlH_4$ in dry ether, or catalytic hydrogenation with sodium in alcohol (Mendius reduction).

Concept used. **Nitrile reduction** adds two H atoms across each of the two $C-N$ π bonds, converting $R-C\equiv N$ into $R-CH_2-NH_2$ (a 1° amine that has one more carbon than the parent halide).

Step 1. $R-C\equiv N + 4\,[H] \xrightarrow{LiAlH_4\ /\ \text{ether}} R-CH_2-NH_2$ (clean, single product).

Step 2. Alternative: $R-C\equiv N + 4\,[H] \xrightarrow{Na\ /\ C_2H_5OH} R-CH_2-NH_2$ (Mendius reduction).

Step 3. Catalytic hydrogenation (H_2/Ni, Pd, or Pt) also works but can over-reduce in some cases.

> **Final Answer:** $LiAlH_4$ in ether (or Na/C_2H_5OH) reduces nitriles cleanly to 1° amines.

☞ **Choose your reductant by carbon-count target**

Nitrile $\rightarrow$ amine: same carbon count as the nitrile, but $+1$ C relative to the alkyl halide it came from. So $R-X \longrightarrow R-CN \longrightarrow R-CH_2-NH_2$ adds one CH_2.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Hydride-delivery angle. A nitrile's $C{\equiv}N$ triple bond is reduced in two stages: first to an imine $R{-}CH{=}NH$, then to the amine $R{-}CH_2{-}NH_2$. Lithium aluminium hydride is strong enough to push through both steps in a single ether solution, with no isolation of the imine intermediate, and gives the primary amine cleanly. The Mendius alternative (Na in ethanol) is the cheaper bench-scale option used in pre-hydride laboratory practice. Either way, the product is the primary amine $R{-}CH_2{-}NH_2$.

Final Answer: $LiAlH_4$ in ether (or Na/C_2H_5OH).

Q 9.42 **Give the structure of 'A' in the following reaction.**

$$\text{4-methyl-2-nitroaniline} \xrightarrow[\text{(ii) } H_3PO_2,\ H_2O]{\text{(i) } NaNO_2{+}HCl,\ 273\text{-}278\ \text{K}} A.$$

(The substrate has CH_3 at C-4, NO_2 at C-2, NH_2 at C-1 of benzene.)

SOLUTION

Answer: 'A' is **3-nitrotoluene** (m-nitrotoluene), $CH_3{-}C_6H_4{-}NO_2$ with NO_2 at the meta position relative to CH_3.

Concept used. Diazotisation at $0-5\,^\circ C$ ($273-278$ K) converts $Ar{-}NH_2$ to $Ar{-}N_2^+$; subsequent reduction with H_3PO_2/H_2O replaces $-N_2^+$ by $-H$ (deamination). The starting material has CH_3 at C-4 and NO_2 at C-2 *relative to the* NH_2 *group at C-1*. After deamination at C-1, only CH_3 and NO_2 remain on the ring, CH_3 at the original C-4 position and NO_2 at the original C-2 — but after dropping NH_2, the ring is renumbered so that the substituents now end up *meta* to each other.

Step 1. Diazotisation: $Ar{-}NH_2 + NaNO_2 + 2\,HCl \longrightarrow Ar{-}N_2^+\,Cl^- + NaCl + 2\,H_2O$ at $273-278$ K.

Step 2. Reduction: $Ar{-}N_2^+\,Cl^- + H_3PO_2 + H_2O \longrightarrow Ar{-}H + N_2 + H_3PO_3 + HCl$.

Step 3. Ring map: C-1 was NH_2, C-2 was NO_2, C-4 was CH_3. After removing NH_2, the remaining substituents are NO_2 and CH_3 on positions that translate to 1,3 (meta).

Final Answer: 'A' = 3-nitrotoluene (m-nitrotoluene), m-$CH_3{-}C_6H_4{-}NO_2$.

☞ **Deamination as a positioning tool**

The $-NH_2$ here is sacrificed (deaminated) to lock a m-orientation between NO_2 and CH_3 that would be otherwise hard to install via direct nitration of toluene (which gives mostly o/p).

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Track-the-substituents angle. The substrate has three ring substituents: NH_2 at C-1, NO_2 at C-2 and CH_3 at C-4 of benzene. Step (i) diazotises the amine to $-N_2^+\,Cl^-$ at C-1, holding it at the cold $0-5\,^\circ C$ window that stabilises the aryl diazonium salt. Step (ii) hands off a hydrogen atom from H_3PO_2 to the aryl radical, releasing N_2 and replacing $-N_2^+$ by $-H$. So NH_2 at C-1 simply disappears. What is left is a benzene ring with NO_2 (originally at C-2) and CH_3 (originally at C-4) — which sit *meta* to each other in the renumbered product. The product is 3-nitrotoluene.

> **Final Answer:** 3-nitrotoluene (m-nitrotoluene).

Q 9.43 What is Hinsberg reagent?

SOLUTION

Answer: **Hinsberg reagent** is benzenesulphonyl chloride, $C_6H_5-SO_2Cl$.
Concept used. The **Hinsberg test** uses $C_6H_5SO_2Cl$ to distinguish 1°, 2° and 3° amines. The reagent's $S(=O)_2$ is a strong electrophile; an amine's lone pair displaces Cl^- to give a sulphonamide.

Step 1. 1° amine: $R-NH_2 + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_2NHR$. The N-H is acidic (sulphonyl is strongly EW) $\Rightarrow$ soluble in alkali.

Step 2. 2° amine: $R_2NH + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_2NR_2$. No N-H left $\Rightarrow$ insoluble in alkali.

Step 3. 3° amine: no N-H to lose $\Rightarrow$ does not react.

> **Final Answer:** Hinsberg reagent $=$ $C_6H_5SO_2Cl$ (benzenesulphonyl chloride); used to distinguish $1^\circ/2^\circ/3^\circ$ amines by alkali solubility.

☞ Three-tube observation table

Tube 1 (1°): clear solution that turns cloudy on acidifying (sulphonamide precipitates back). Tube 2 (2°): solid that stays as a solid even on adding NaOH (no acidic $N-H$). Tube 3 (3°): unreacted amine layer floats on top — no sulphonamide forms.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Reagent-plus-pattern angle. Hinsberg's reagent is benzenesulphonyl chloride, $C_6H_5{-}SO_2{-}Cl$. The strongly electrophilic sulphonyl sulphur is attacked by the amine lone pair, displacing chloride and producing a sulphonamide whose properties diagnose the amine class.

With a primary amine, the resulting $C_6H_5{-}SO_2{-}NHR$ retains an $N{-}H$ that is rendered acidic by the two electron-withdrawing oxygens on sulphur, so $NaOH$ deprotonates it and the salt dissolves. With a secondary amine, the sulphonamide $C_6H_5{-}SO_2{-}NR_2$ has no $N{-}H$ left and stays as an alkali-insoluble solid. A tertiary amine has no $N{-}H$ at the outset and does not even react. Comparing the three test tubes fixes the class of an unknown amine on the bench.

> **Final Answer:** Hinsberg reagent is $C_6H_5SO_2Cl$.

Q 9.44 Why is benzene diazonium chloride not stored and is used immediately after its preparation?

SOLUTION

Answer: Benzene diazonium chloride $C_6H_5{-}N_2{}^+\,Cl^-$ is **thermally unstable** above $5\,^\circ C$. On warming, even gently, it decomposes to give phenol, N_2 and HCl (or chlorobenzene if dry); on prolonged storage even in solution it slowly decomposes by the same routes. So it must be prepared at $0-5\,^\circ C$ and used immediately in the downstream reaction.

Concept used. The arenium-stabilised $Ar{-}N{\equiv}N^+$ cation is more stable than its aliphatic cousin (which dies on contact with water), but at higher temperatures the loss of N_2 becomes spontaneous because N_2 is an outstanding leaving group.

Step 1. In water, $>5\,^\circ C$: $C_6H_5{-}N_2{}^+\,Cl^- + H_2O \longrightarrow C_6H_5{-}OH + N_2 + HCl$.

Step 2. In dry solid form, on standing: $C_6H_5{-}N_2{}^+\,Cl^- \longrightarrow C_6H_5{-}Cl + N_2$ (the dry salt can even detonate).

> **Final Answer:** Thermal instability of $Ar{-}N_2{}^+$; prepared cold ($0-5\,^\circ C$) and used at once to avoid loss of N_2 to give phenol or chlorobenzene.

☞ **The $0-5\,^\circ C$ rule**

The diazotisation temperature window is a favourite MCQ trap. Aliphatic diazotisation: room temperature (cation dies anyway). Aromatic diazotisation: $0-5\,^\circ C$ (cold ice-bath).

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Thermal-decomposition angle. A diazonium salt is a delicate species; the bond linking the aryl ring to the $-\mathrm{N}{\equiv}\mathrm{N}^{+}$ group breaks easily because N_2 is one of the most thermodynamically favourable leaving groups. In an aromatic compound, ring resonance partially stabilises the cation, but only at very low temperature. Warming above $\sim 5\,^{\circ}\mathrm{C}$ supplies enough thermal energy to eject N_2, and in aqueous solution water immediately traps the aryl cation as phenol. So the standard recipe is to diazotise in an ice bath at $0-5\,^{\circ}\mathrm{C}$ and pipe the cold solution directly into the next reaction — never to bottle and store.

> **Final Answer:** Diazonium chloride is unstable above $5\,^{\circ}\mathrm{C}$; preparation and use must be back-to-back at $0-5\,^{\circ}\mathrm{C}$.

Q 9.45 Why does acetylation of $-\mathrm{NH}_2$ group of aniline reduce its activating effect?

SOLUTION

Answer: The N lone pair of aniline, originally free to push into the ring (strong $+M$ activator), is now shared with the carbonyl O via the amide resonance $\mathrm{R{-}NH{-}CO{-}R_2} \longleftrightarrow \mathrm{R{-}NH^{+}{=}C(O^{-}){-}R_2}$. The lone pair becomes less available to the ring $\Rightarrow$ ring activation drops sharply.

Concept used. The amide carbonyl is a π-acceptor that competes with the benzene ring for the nitrogen lone pair. Resonance with $\mathrm{C{=}O}$ is energetically more favourable than resonance with the benzene ring (carbonyl is more polarisable), so most of the lone pair is locked into the $\mathrm{N{-}C{=}O}$ system.

Step 1. In aniline: lone pair $\mathrm{N} \longrightarrow \mathrm{ring}$ $(+M)$; ring activation $\approx 10^{6}\times$ benzene.

Step 2. In acetanilide: lone pair is shared between $\mathrm{N} \longrightarrow \mathrm{ring}$ and $\mathrm{N} \longrightarrow \mathrm{C{=}O}$; the carbonyl wins the larger share.

Step 3. Net: $\mathrm{NHCOCH_3}$ is still an activator (mild) but much weaker than $\mathrm{NH_2}$ (strong).

> **Final Answer:** Amide resonance with $\mathrm{C{=}O}$ pulls the lone pair off the ring, dropping the activating power of $-\mathrm{NHCOCH_3}$ relative to $-\mathrm{NH_2}$.

☞ Why we acetylate before nitration

This same effect is why acetylation tames aniline before nitration: a calmer ring tolerates the harsh nitrating mixture without oxidation, and the o/p-director status is preserved.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Lone-pair-competition angle. In free aniline the nitrogen lone pair is entirely available to push into the benzene ring, which is why $-NH_2$ is a powerful o/p-directing activator. Acylation grafts a carbonyl onto the nitrogen, and the same lone pair now has two competitors — the benzene ring and the carbonyl oxygen. The carbonyl wins the larger share because amide resonance ($N-C{=}O \longleftrightarrow N^{+}{=}C-O^{-}$) is highly stabilising; the ring loses most of its lone-pair contribution and therefore most of its activation. Acetanilide is still an activator but only mildly so, which is why nitration of acetanilide can be controlled to give predominantly the para product without ring oxidation.

> **Final Answer:** Amide resonance steals the lone pair from the ring, lowering activation.

Q 9.46 Explain why $MeNH_2$ is a stronger base than $MeOH$.

SOLUTION

Concept used. Basicity (pK_b) is measured by how readily the heteroatom's lone pair grabs H^+. The more *available* the lone pair (low electronegativity, good solvation of the resulting cation), the stronger the base.

Step 1. Electronegativities: $\chi(N) = 3.04$, $\chi(O) = 3.44$.

Step 2. Since O holds its lone pair more tightly than N, methylamine's N donates its lone pair to H^+ more readily than methanol's O does.

Step 3. Conjugate-acid view: $CH_3NH_3^+$ ($pK_a \approx 10.6$) is much weaker than $CH_3OH_2^+$ ($pK_a \approx -2$). Weaker conjugate acid $\Rightarrow$ stronger base.

> **Final Answer:** N is less electronegative than O, so its lone pair is more available for protonation; hence $MeNH_2$ is the stronger base.

☞ **Conjugate-acid mnemonic**

Stronger base $\Leftrightarrow$ weaker conjugate acid. $CH_3NH_3^+$ has $pK_a \approx 10.6$ (weak acid), while $CH_3OH_2^+$ has $pK_a \approx -2$ (strong acid). The ~ 12 unit gap mirrors the basicity gap exactly.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Electronegativity angle. The deciding factor for a neutral heteroatom base is how tightly the atom holds its lone pair. Electronegativity is the direct proxy. Nitrogen sits at

$\chi = 3.04$ on the Pauling scale; oxygen at $\chi = 3.44$. Lower electronegativity means a more diffuse, more donatable lone pair, so methylamine's nitrogen donates electrons to H^+ far more readily than methanol's oxygen does.
Cross-check with conjugate-acid strengths: $CH_3NH_3^+$ has $pK_a \approx 10.6$, while $CH_3OH_2^+$ has $pK_a \approx -2$. Methanol's conjugate acid is roughly 10^{12} times stronger, so methanol itself is $\sim 10^{12}$ times weaker as a base. The pattern generalises across the table — amines beat alcohols of the same skeleton in basicity by many orders of magnitude.

> **Final Answer:** N lone pair is more available than O lone pair, so $MeNH_2 \gg MeOH$ as a base.

Q 9.47 What is the role of pyridine in the acylation reaction of amines?

SOLUTION

Answer: Pyridine acts as a **base** that neutralises the HCl (or CH_3COOH) liberated during acylation, keeping the amine deprotonated (and therefore nucleophilic) and pushing the equilibrium towards the amide product. Pyridine also catalyses the reaction via a nucleophilic-catalysis pathway (N-acyl pyridinium intermediate).
Concept used. If the by-product acid (HCl from acyl chloride or CH_3COOH from anhydride) is allowed to accumulate, it would protonate the amine to $R{-}NH_3^+$, which has no lone pair available for further attack and so the acylation stalls. Pyridine sops up that acid as $C_5H_5N \cdot H^+ X^-$.

Step 1. Acylation: $R{-}NH_2 + R_2{-}COCl \longrightarrow R{-}NH{-}CO{-}R_2 + HCl$.

Step 2. Pyridine traps HCl: $HCl + C_5H_5N \longrightarrow C_5H_5NH^+\,Cl^-$.

Step 3. Without pyridine: $HCl + R{-}NH_2 \longrightarrow R{-}NH_3^+\,Cl^-$, the salt is unreactive.

> **Final Answer:** Pyridine is the acid scavenger (and a mild nucleophilic catalyst); it keeps the amine free and pulls the acylation forward.

☞ **Other base options**
Et_3N (triethylamine) and Na_2CO_3 play the same role. NCERT lists pyridine as the canonical choice.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Acid-scavenger angle. Every acylation of an amine produces an acidic by-product — HCl when the acyl source is an acid chloride, carboxylic acid when it is an anhydride. If

that acid is left in solution it protonates the amine nucleophile to $R{-}NH_3^+$, which loses its lone pair and stops attacking the carbonyl. Pyridine, with $pK_b \approx 8.8$, is basic enough to grab the proton from HCl but not basic enough to compete with the amine for the acyl electrophile; it also weakly catalyses the acylation through a short-lived N-acyl-pyridinium intermediate. So pyridine keeps the reaction running cleanly to the amide.

Final Answer: Pyridine removes the acid by-product, keeping the amine free.

Q 9.48 Under what reaction conditions (acidic/basic), the coupling reaction of aryldiazonium chloride with aniline is carried out?

SOLUTION

Answer: Mildly acidic (pH $\approx 4-5$) — or equivalently very weakly basic but *not* alkaline.

Concept used. Two species must coexist for the coupling to work: (a) the aryl diazonium cation ArN_2^+ (stable only below $5\,^\circ C$ and in mildly acidic medium; strong base destroys it as diazoate $Ar{-}N{=}N{-}O^-$), and (b) the nucleophilic free amine $ArNH_2$ (lost under strongly acidic conditions because $-NH_2$ is protonated to the unreactive $-NH_3^+$).

Step 1. In strong acid: $ArNH_2 + H^+ \longrightarrow ArNH_3^+$, no lone pair, no coupling.

Step 2. In strong base: $ArN_2^+ + OH^- \longrightarrow Ar{-}N{=}N{-}OH \longrightarrow Ar{-}N{=}N{-}O^-$ (diazoate), no electrophile.

Step 3. At pH $\sim 4-5$ (mildly acidic / weakly basic), enough free aniline (lone pair) coexists with enough ArN_2^+ to react.

Final Answer: Mildly acidic conditions (pH 4–5); the medium keeps both partners alive for coupling.

☞ Phenol coupling is different

With phenol, mild base is preferred (pH 9–10): OH^- deprotonates $-OH$ to the more nucleophilic phenoxide $-O^-$, and the diazonium cation is still alive at that mildly basic pH.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Both-must-survive angle. The trick to picking the right pH for azo coupling is to ask which form of each partner is catalytically active and what range of pH lets both forms coexist. For aniline coupling the diazonium needs a mildly acidic medium (so it does not convert to the unreactive diazoate), and the aniline nitrogen needs to keep its lone pair (so the medium cannot be strongly acidic enough to protonate the amine to $ArNH_3^+$). Both conditions are met at pH $\approx 4-5$, which the NCERT calls "mild basic / weak acidic". So coupling of aryldiazonium chloride with aniline is done in mild acid.

> **Final Answer:** Mildly acidic ($\sim$ pH 4–5) conditions.

Q 9.49 **Predict the product of reaction of aniline with bromine in a non-polar solvent such as CS_2.**

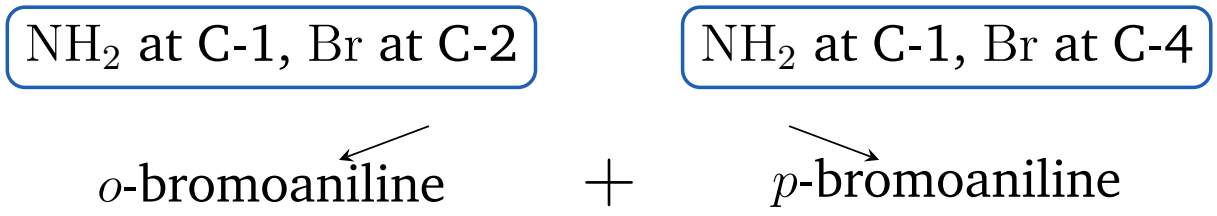
SOLUTION

Product: A mixture of **2-bromoaniline** and **4-bromoaniline** (mainly p-bromoaniline).
Concept used. Aniline is strongly activating; in *aqueous* bromine water it gives 2,4,6-tribromoaniline at once. In a *non-polar* solvent (CS_2) the $-NH_2$ is not protonated and the reaction is gentler — bromination stops at the monosubstituted stage, giving mainly p-bromoaniline plus some o-bromoaniline.

Step 1. Generate Br^+: Br_2 polarises on approach to the electron-rich ring.

Step 2. EAS at o/p: $-NH_2$ is an o/p-director by $+M$.

Step 3. In CS_2, only one Br installs $\Rightarrow$ mono-bromination at o and p.



> **Final Answer:** Mixture of 2-bromoaniline and 4-bromoaniline (p-product dominant).

☞ **Aqueous vs. CS_2**
Water solvates Br^+ less and lets all three $o/o'/p$ positions react $\Rightarrow$ tribromoaniline. CS_2 is non-polar and gentler $\Rightarrow$ mono-bromination only.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Solvent-control angle. The two canonical bromination outcomes of aniline are dictated entirely by solvent. In water, Br_2 is heterolytically polarised by the highly solvating medium, releasing Br^+ that finds the aniline ring extremely electron-rich at three positions (*ortho*, *ortho'* and *para*). All three positions react, giving 2,4,6-tribromoaniline as a white precipitate — the standard qualitative test for aniline.
Switching the solvent to CS_2 removes the polarising medium. Br^+ is generated only sluggishly, and the lone pair on $-NH_2$ is not protonated, so the ring is still activated but substitution slows down dramatically. The first bromine installs at the activated o or p position, after which the ring is less reactive and the second/third Br^+ attack is suppressed. The isolable products are 2-bromoaniline (minor) and 4-bromoaniline (major), the latter favoured for steric reasons over the *ortho* positions.

> **Final Answer:** 2-bromoaniline (minor) + 4-bromoaniline (major), monobromination.

Q 9.50 **Arrange the following compounds in increasing order of dipole moment.**
$CH_3CH_2CH_3$, $CH_3CH_2NH_2$, CH_3CH_2OH

SOLUTION

Order: $CH_3CH_2CH_3 < CH_3CH_2NH_2 < CH_3CH_2OH$.
Concept used. Dipole moment μ scales with the **electronegativity difference** across the polar bond. $\chi(C) = 2.55$, $\chi(N) = 3.04$, $\chi(O) = 3.44$. The C–O dipole ($\Delta\chi = 0.89$) is much larger than the C–N dipole ($\Delta\chi = 0.49$); the C–C bond in propane has $\Delta\chi = 0$, so propane is essentially apolar.

Step 1. Propane: only C–H and C–C bonds; $\mu \approx 0.08$ D.

Step 2. Ethylamine: C–N and N–H polar bonds; $\mu \approx 1.22$ D.

Step 3. Ethanol: C–O and O–H polar bonds; $\mu \approx 1.69$ D.

> **Final Answer:** $CH_3CH_2CH_3 < CH_3CH_2NH_2 < CH_3CH_2OH$.

☞ **Why ethanol still wins despite N–H count**

Ethylamine has two N–H bonds versus ethanol's one O–H, yet ethanol is more polar. The reason: the per-bond dipole on O–H ($\Delta\chi = 1.24$) dwarfs N–H ($\Delta\chi = 0.84$), and the C–O dipole alone outguns the C–N dipole.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Electronegativity-difference angle. Molecular dipole moment is the vector sum of bond dipoles, so it scales with the electronegativity difference $\Delta\chi$ across each polar bond and with the geometry that decides whether they add or cancel. For the three molecules here the geometry is similar (terminal heteroatom on an ethyl chain), so the per-bond dipole reads almost directly into the molecular dipole.
Propane has only $\mathrm{C{-}C}$ and $\mathrm{C{-}H}$ bonds, both with $\Delta\chi$ near zero, so its dipole moment is essentially zero ($\sim 0.08\,\mathrm{D}$). Ethylamine introduces a $\mathrm{C{-}N}$ bond ($\Delta\chi = 0.49$) and two $\mathrm{N{-}H}$ bonds ($\Delta\chi = 0.84$), giving $\mu \approx 1.22\,\mathrm{D}$. Ethanol has a $\mathrm{C{-}O}$ bond ($\Delta\chi = 0.89$) and an $\mathrm{O{-}H}$ bond ($\Delta\chi = 1.24$), each more polar than its nitrogen counterpart, giving $\mu \approx 1.69\,\mathrm{D}$. So the dipole order matches the electronegativity-difference order exactly: propane $<$ ethylamine $<$ ethanol.

Final Answer: $\mathrm{C_3H_8} < \mathrm{C_2H_5NH_2} < \mathrm{C_2H_5OH}$.

Q 9.51 What is the structure and IUPAC name of the compound, allyl amine?

SOLUTION

Answer: Structure — $\mathrm{CH_2{=}CH{-}CH_2{-}NH_2}$. IUPAC name — **prop-2-en-1-amine**.
Concept used. The common name "allyl" is the $\mathrm{CH_2{=}CH{-}CH_2^-}$ group; adding $-\mathrm{NH_2}$ gives allylamine. To name it by IUPAC: longest chain that includes the amine carbon is propene; amine on C-1, double bond between C-2 and C-3 $\Rightarrow$ prop-2-en-1-amine.

Step 1. Structural drawing: $\mathrm{H_2C{=}CH{-}CH_2{-}NH_2}$ (3 carbons, terminal $\mathrm{NH_2}$, terminal $\mathrm{C{=}C}$).

Step 2. Functional priority: amine $>$ alkene, so the chain is numbered from the amine end.

Step 3. C-1: $\mathrm{CH_2{-}NH_2}$; C-2 and C-3: $\mathrm{CH{=}CH_2}$.

Step 4. Locants: "2-en" for the double bond, "1-amine" for $-\mathrm{NH_2}$ $\Rightarrow$ prop-2-en-1-amine.

Final Answer: Allyl amine $= \mathrm{CH_2{=}CH{-}CH_2{-}NH_2}$ = prop-2-en-1-amine.

☞ **Allyl vs. vinyl**
"Allyl" is $\mathrm{CH_2{=}CH{-}CH_2^-}$ (carbon between $\mathrm{NH_2}$ and $\mathrm{C{=}C}$); "vinyl" is $\mathrm{CH_2{=}CH^-}$ (no buffer carbon). Vinylamine $\mathrm{CH_2{=}CH{-}NH_2}$ is unstable and tautomerises.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Common-to-IUPAC angle. The trivial name allylamine encodes the connectivity: an allyl group $CH_2{=}CH{-}CH_2{}^-$ on nitrogen, giving the three-carbon primary amine $CH_2{=}CH{-}CH_2{-}NH_2$. To convert to IUPAC, pick the longest chain that includes the amine carbon — here, the three-carbon propene chain — and number it so the principal characteristic group (the amine) gets the lower locant. The amine ends up on C-1 and the double bond between C-2 and C-3, giving prop-2-en-1-amine.

Final Answer: $CH_2{=}CH{-}CH_2{-}NH_2$; prop-2-en-1-amine.

Q 9.52 **Write down the IUPAC name of $C_6H_5{-}N(CH_3)_2$ (N,N-dimethyl benzene amine).**

SOLUTION

Answer: **N,N-dimethylbenzenamine** (also written N,N-dimethylaniline).
Concept used. For an aryl amine, the IUPAC name uses "benzenamine" (or the retained name "aniline") as the parent, with N-substituents prefixed by italic "N-". The compound $C_6H_5{-}N(CH_3)_2$ has two methyl groups on nitrogen ⇒ "N,N-dimethylbenzenamine".

Step 1. Parent: benzene with $-NH_2$ = benzenamine (or aniline).

Step 2. N-substituents: two methyls on nitrogen ⇒ "N,N-dimethyl".

Step 3. Full IUPAC name: N,N-dimethylbenzenamine; equivalent common name: N,N-dimethylaniline.

Final Answer: N,N-dimethylbenzenamine (= N,N-dimethylaniline).

☞ **Aniline is a retained IUPAC name**

The CAS and recent IUPAC rules retain "aniline" for $C_6H_5{-}NH_2$, so "N,N-dimethylaniline" is also accepted. "Benzenamine" is the strict 1993 IUPAC name.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

N-locant angle. An aniline derivative with all substituents on the nitrogen (rather than on the ring) is named by leaving the parent as benzenamine and prefixing the substituents with the locant "N". Two methyl groups on the nitrogen of aniline give N,N-dimethylbenzenamine (or, using the retained name, N,N-dimethylaniline). The italicised N's are required to distinguish nitrogen substitution from C-ring substitution.

Final Answer: N,N-dimethylbenzenamine.

Q 9.53 **A compound Z with molecular formula C_3H_9N reacts with $C_6H_5SO_2Cl$ to give a solid, insoluble in alkali. Identify Z.**

SOLUTION

Answer: Z is **ethylmethylamine**, $CH_3-NH-C_2H_5$, a 2° amine.

Concept used. Behaviour with the Hinsberg reagent ($C_6H_5SO_2Cl$) is a fingerprint of amine class. (a) 1° amine gives an alkali-soluble sulphonamide (acidic $N-H$). (b) 2° amine gives an alkali-insoluble sulphonamide (no $N-H$). (c) 3° amine does not react.

Step 1. Molecular formula C_3H_9N has degree of unsaturation $= 0$, so Z is acyclic and saturated.

Step 2. Possible structures: n-$C_3H_7-NH_2$ (1°), $(CH_3)_2CH-NH_2$ (1°), $CH_3-NH-C_2H_5$ (2°), $(CH_3)_3N$ (3°).

Step 3. "Reacts with Hinsberg" $\Rightarrow$ not 3°. "Solid insoluble in alkali" $\Rightarrow$ 2° amine.

Step 4. The only C_3H_9N 2° amine is ethylmethylamine $CH_3-NH-C_2H_5$.

Final Answer: Z is ethylmethylamine, $CH_3-NH-C_2H_5$, which gives N-ethyl-N-methylbenzene sulphonamide (alkali-insoluble).

✗ Don't say "n-propylamine"!

A primary amine like n-propylamine or isopropylamine would have given an alkali-*soluble* sulphonamide because of the residual acidic $N-H$. "Alkali-insoluble" is the unique signature of a secondary amine, so the only valid C_3H_9N answer is ethylmethylamine.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Class-then-isomer angle. Approach this as a two-stage deduction. First, the Hinsberg behaviour pins the class: a sulphonamide that is *insoluble in alkali* can only come from a secondary amine, because primary amines yield alkali-soluble sulphonamides (acidic $N-H$) and tertiary amines do not react with Hinsberg's reagent at all.

Second, the molecular formula C_3H_9N has degree of unsaturation zero, so the parent is acyclic and saturated. The four possible isomers are n-propylamine, isopropylamine, N-methylethylamine, and trimethylamine. The first two are primary, trimethylamine is tertiary, leaving N-methylethylamine $CH_3-NH-C_2H_5$ as the only C_3H_9N secondary

amine. That isomer fits every clue: it reacts with $PhSO_2Cl$ to give N-ethyl-N-methylbenzene sulphonamide, which has no acidic $N-H$ and so stays insoluble in alkali.

Final Answer: Z = ethylmethylamine $CH_3-NH-C_2H_5$.

Q 9.54 **A primary amine $R-NH_2$ can be reacted with CH_3-X to get a secondary amine $R-NHCH_3$, but the only disadvantage is that 3° amine and quaternary ammonium salts are also obtained as side products. Suggest a method where $R-NH_2$ forms only the 2° amine.**

SOLUTION

Method: Use the carbylamine reaction followed by catalytic hydrogenation.

$$R-NH_2 \xrightarrow{CHCl_3\,/\,KOH} R-NC \xrightarrow{H_2\,/\,Pd} R-NHCH_3$$

Concept used. The carbylamine route gives the 2° amine $R-NH-CH_3$ in two clean steps: (a) formation of alkyl isocyanide $R-NC$ from $R-NH_2$ with $CHCl_3$/alc. KOH (the two $N-H$ are replaced by a single $N=C$ bond); (b) catalytic hydrogenation of $R-NC$ over Pd reduces the $N=C$ bond to $N-CH_2^- = N-CH_3$ (because the carbon already carries no other H), giving the 2° amine without any further alkylation possible.

Step 1. Step 1 (carbylamine): $R-NH_2 + CHCl_3 + 3\,KOH \longrightarrow R-NC + 3\,KCl + 3\,H_2O$.

Step 2. Step 2 (reduction): $R-NC + 2\,H_2 \xrightarrow{Pd} R-NH-CH_3$.

Step 3. Net: $R-NH_2 \longrightarrow R-NH-CH_3$, exactly one methyl added on N, no 3° or 4° side products.

Final Answer: $R-NH_2 \xrightarrow{CHCl_3/KOH} R-NC \xrightarrow{H_2/Pd} R-NHCH_3$ stops cleanly at the 2° amine.

☞ **Why this beats direct alkylation**

Direct alkylation cannot self-stop at 2° because the freshly formed $R-NH-CH_3$ is even more nucleophilic than $R-NH_2$; the carbylamine route bypasses that runaway by installing the methyl through an entirely different functional group.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Self-stopping-route angle. The reason direct alkylation of a primary amine cannot be stopped at the secondary stage is that each newly-formed amine is more nucleophilic than the one that came before, so methylation just keeps going. The carbylamine workaround sidesteps this by hand-installing the methyl as an isocyanide in two non-amine steps. First, chloroform plus alcoholic potash converts $\mathrm{R{-}NH_2}$ to the foul-smelling alkyl isocyanide $\mathrm{R{-}NC}$ (a $\mathrm{C{=}N}$ bond, not a nucleophilic amine). Second, catalytic hydrogenation reduces that triple bond to a single $\mathrm{N{-}CH_3}$, giving exactly the 2° amine and stopping there because the new amine has no available carbon nucleophile to over-react with. Cleanly single-substituted.

Final Answer: Carbylamine ($\mathrm{CHCl_3/KOH}$) then $\mathrm{H_2/Pd}$.

Q 9.55 **Complete the following reaction:**

$$\textbf{Phenol} \xrightarrow[\mathrm{OH^-}]{\mathrm{ArN_2^+\,Cl^-}} ?$$

SOLUTION

Product: p-Hydroxyazobenzene (when $\mathrm{Ar} = \mathrm{C_6H_5}$), the orange azo dye $\mathrm{HO{-}C_6H_4{-}N{=}N{-}C_6H_5}$.

Concept used. **Azo coupling**: in mild alkaline medium, phenol is deprotonated to the highly activated phenoxide ion $\mathrm{C_6H_5O^-}$, which attacks the weak electrophile $\mathrm{ArN_2^+}$ at its *para* position to give an azo compound. The orange/yellow colour comes from the extended π-conjugated $\mathrm{Ar{-}N{=}N{-}Ar_2}$ chromophore.

Step 1. Deprotonation: $\mathrm{C_6H_5OH + OH^- \longrightarrow C_6H_5O^- + H_2O}$.

Step 2. EAS coupling: $\mathrm{ArN_2^+ + C_6H_5O^- \longrightarrow p\text{-}HO{-}C_6H_4{-}N{=}N{-}Ar + H^+}$.

Step 3. For the generic aryl, the product is p-aryloxoazobenzene; for $\mathrm{Ar} = \mathrm{C_6H_5}$, p-hydroxyazobenzene.

$$\text{Phenol } \mathrm{C_6H_5{-}OH} \xrightarrow{\mathrm{ArN_2^+\,Cl^-/OH^-}} \underset{\text{(orange azo dye)}}{p\text{-}\mathrm{HO{-}C_6H_4{-}N{=}N{-}Ar}}$$

Final Answer: Product = p-hydroxyazobenzene, an orange azo dye, formed by para coupling of phenoxide with aryl diazonium cation.

☞ Why para, not ortho

The phenoxide is so highly activated that both o and p positions are reactive, but para wins on steric grounds (no clash between the bulky diazonium and the $-O^-$).

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Phenoxide-EAS angle. Azo coupling needs a strongly electron-rich aromatic partner because the diazonium cation is a weak electrophile. Phenol meets that bar barely; phenoxide $C_6H_5O^-$ blows past it, with the formal negative charge on oxygen flooding the ring with electron density at the o and p positions. Mildly alkaline medium is therefore ideal: it generates the phenoxide while still being mild enough not to destroy the diazonium as the unreactive diazoate. The product is the para-coupled azo compound $HO-C_6H_4-N=N-Ar$, with the extended π system that gives azo dyes their characteristic orange to red colour.

Final Answer: p-hydroxyazobenzene, the orange para azo dye.

Q 9.56 Why is aniline soluble in aqueous HCl?

SOLUTION

Concept used. Although aniline itself is a sparingly soluble oily liquid (the $-NH_2$ lone pair is partly delocalised into the ring), its conjugate acid **anilinium chloride** $C_6H_5NH_3^+\,Cl^-$ is a fully ionic salt — it dissolves in water just as ammonium chloride does.

Step 1. $C_6H_5NH_2 + HCl \longrightarrow C_6H_5NH_3^+\,Cl^-$ (proton transfer).

Step 2. The anilinium cation is hydrated by water (H-bonds to the three $N-H$ bonds and ion–dipole attractions).

Step 3. Cl^- is independently hydrated $\Rightarrow$ the salt dissolves freely in aqueous HCl.

Final Answer: Aniline + HCl gives the water-soluble salt anilinium chloride, hence the apparent solubility in aqueous HCl.

☞ Same logic, different molecule

Carboxylic acids dissolve in aqueous NaOH for the mirror reason: salt formation. Acid/base solubility tests rely on this.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Salt-formation angle. The trick to seeing why aniline "dissolves" in HCl is to separate the free amine from its protonated form. Free aniline is a neutral, oily, weakly polar molecule held in water mainly by a single $N{-}H\cdots O$ contact; it spreads as droplets on the water surface and is only sparingly soluble.
Add HCl and the picture changes. Aniline is still a Brønsted base (a feeble one, $pK_b \approx 9.4$) but HCl is a strong acid, so proton transfer is essentially complete: $C_6H_5NH_2 + HCl \longrightarrow C_6H_5NH_3^+\,Cl^-$. The product is an ionic salt — a fully charged anilinium cation hydrated by water (ion–dipole plus three $N{-}H\cdots O$ hydrogen bonds) and a chloride anion that water hydrates independently. Ionic salts dissolve readily in water, so the apparent dissolution of aniline in aqueous HCl is really the dissolution of the salt anilinium chloride.

Final Answer: Aniline forms water-soluble anilinium chloride with HCl.

Q 9.57 Suggest a route by which the following conversion can be accomplished: cyclohexanecarboxamide → N-methylcyclohexylamine (c-$C_6H_{11}{-}NH{-}CH_3$).

SOLUTION

Strategy. Hoffmann bromamide → carbylamine → catalytic hydrogenation.

(1) c-$C_6H_{11}{-}CONH_2 \xrightarrow{Br_2/KOH}$ c-$C_6H_{11}{-}NH_2$ (Hoffmann, -1 C).

(2) c-$C_6H_{11}{-}NH_2 \xrightarrow{CHCl_3/KOH}$ c-$C_6H_{11}{-}NC$ (carbylamine).

(3) c-$C_6H_{11}{-}NC \xrightarrow{H_2/Pd}$ c-$C_6H_{11}{-}NH{-}CH_3$ (reduction).

Concept used. Two named reactions string together: (a) Hoffmann bromamide chops the carbonyl off the amide and gives the 1° amine cyclohexylamine; (b) Carbylamine grafts a single methyl-equivalent ($-NC$) onto N which is then reduced to $-NH{-}CH_3$. Cleaner than direct methylation, which over-alkylates.

Step 1. Step 1: $R{-}CONH_2 + Br_2 + 4\,KOH \longrightarrow R{-}NH_2 + K_2CO_3 + 2\,KBr + 2\,H_2O$ where R = cyclohexyl.

Step 2. Step 2: $R{-}NH_2 + CHCl_3 + 3\,KOH \longrightarrow R{-}NC + 3\,KCl + 3\,H_2O$.

Step 3. Step 3: $R{-}NC + 2\,H_2 \xrightarrow{Pd} R{-}NH{-}CH_3$.

Final Answer: Cyclohexanecarboxamide $\xrightarrow{Br_2/KOH}$ cyclohexylamine $\xrightarrow{CHCl_3/KOH}$ cyclohexylisocyanide $\xrightarrow{H_2/Pd}$ N-methylcyclohexylamine.

☞ **Why not direct methylation**

c-$C_6H_{11}-NH_2 + CH_3I$ would give a mix of $1^\circ/2^\circ/3^\circ/4^\circ$ amines, and is awkward to separate. The carbylamine + reduction route caps at 2° by design.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Two-named-reactions angle. Read the target backwards. N-methylcyclohexylamine has a methyl on a cyclohexyl nitrogen, so the immediate precursor is something that, on reduction, deposits a single CH_3 on the amine nitrogen — the canonical candidate is cyclohexylisocyanide c-$C_6H_{11}-NC$, whose $N{=}C$ bond reduces under H_2/Pd to $N-CH_3$. That isocyanide in turn comes from cyclohexylamine via the carbylamine reaction with $CHCl_3/KOH$. Finally, cyclohexylamine comes from cyclohexanecarboxamide via Hoffmann bromamide degradation, which drops the carbonyl carbon. Three named-reaction steps, clean conversion.

> **Final Answer:** Hoffmann (Br_2/KOH) $\rightarrow$ carbylamine ($CHCl_3/KOH$) $\rightarrow$ reduction (H_2/Pd).

Q 9.58 **Identify A and B in the following reaction:**

$$\textbf{2-(2-chloroethyl)cyclohexan-1-one} \xrightarrow{KCN} A \xrightarrow{H_2/Pd} B.$$

SOLUTION

Answers.

- **A:** 2-(2-cyanoethyl)cyclohexan-1-one — the $-CH_2-CH_2-Cl$ tail of the substrate has been converted to $-CH_2-CH_2-CN$ by S_N2 displacement of Cl^- by CN^-.
- **B:** 2-(3-aminopropyl)cyclohexan-1-one — the nitrile of A has been reduced to a primary amine $-CH_2-CH_2-CH_2-NH_2$ (the chain has gained one CH_2).

Concept used. Two single-step transformations: S_N2 with KCN on a primary alkyl chloride gives a nitrile (chain $+1$ C); H_2/Pd reduces the nitrile to a 1° amine (with no further change in carbon count).

Step 1. Substitution: $R-CH_2-Cl + KCN \longrightarrow R-CH_2-CN + KCl$ (S_N2).

Step 2. Reduction: $R-CH_2-CN + 2\,H_2 \xrightarrow{Pd} R-CH_2-CH_2-NH_2$.

Step 3. The cyclohexanone $C{=}O$ does not reduce under H_2/Pd at room temperature with normal pressure $\Rightarrow$ ketone survives.

Final Answer: A = 2-(2-cyanoethyl)cyclohexan-1-one; B = 2-(3-aminopropyl)cyclohexan-1-one.

☞ **Pd vs. harsher catalysts**

H_2/Pd at mild conditions reduces only the nitrile to amine; the ketone is left untouched. If you wanted to reduce both, you would use $LiAlH_4$ (and end up with an amino-alcohol).

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Two-step-sequence angle. The first arrow over KCN is the textbook substitution that swaps a chloride for a cyanide. The $-CH_2-CH_2-Cl$ tail is a primary alkyl chloride, so the S_N2 goes smoothly, and the cyclohexanone ring is not touched. The product A still bears the ketone but now has a $-CH_2-CH_2-CN$ chain. The second arrow over H_2/Pd reduces the nitrile to a primary amine ($-CN$ becomes $-CH_2-NH_2$, adding one CH_2 to the carbon count). The ring carbonyl survives because the Pd-catalysed conditions are mild enough not to touch a ketone. So B is the amino-ketone with a $-CH_2-CH_2-CH_2-NH_2$ tail.

Final Answer: A = 2-(2-cyanoethyl)cyclohexan−1-one; B = 2-(3-aminopropyl)cyclohexan−1-one.

Q 9.59 How will you carry out the following conversions?
(i) Toluene → *p*-toluidine. (ii) *p*-toluidine diazonium chloride → *p*-toluic acid.

SOLUTION

Part (i): Toluene → *p*-toluidine.

(a) Nitration: $C_6H_5CH_3 \xrightarrow{HNO_3\,/\,H_2SO_4} p\text{-}O_2N-C_6H_4-CH_3$ (with some *o*-isomer; separate by fractional crystallisation).

(b) Reduction: $p\text{-}O_2N-C_6H_4-CH_3 \xrightarrow{Fe\,/\,HCl} p\text{-}H_2N-C_6H_4-CH_3$ (*p*-toluidine).

Part (ii): *p*-toluidine diazonium chloride → *p*-toluic acid ($p\text{-}CH_3-C_6H_4-COOH$).

(a) Sandmeyer (with CuCN/KCN):
$p\text{-}CH_3-C_6H_4-N_2^{+}\,Cl^{-} + CuCN \longrightarrow p\text{-}CH_3-C_6H_4-CN + N_2 + CuCl.$

(b) Acid hydrolysis: $p\text{-}CH_3-C_6H_4-CN + 2\,H_2O \xrightarrow{H^{+}\,/\,heat} p\text{-}CH_3-C_6H_4-COOH + NH_3.$

Concept used. Both halves are textbook: aromatic nitration then reduction (for NH_2); Sandmeyer for $N_2^{+} \longrightarrow CN$ then hydrolysis (for $CN \longrightarrow COOH$).

Final Answer: (i) Toluene $\xrightarrow{HNO_3/H_2SO_4}$ p-nitrotoluene $\xrightarrow{Fe/HCl}$ p-toluidine. (ii) p-Toluidine diazonium chloride $\xrightarrow{CuCN/KCN}$ p-tolunitrile $\xrightarrow{H_2O/H^+,\ \Delta}$ p-toluic acid.

☞ Why p-toluidine from toluene

Toluene's $-CH_3$ is o/p-directing; nitration gives o- and p-nitrotoluene. The p-isomer is separated (higher mp, less soluble), then reduced.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Functional-interconversion angle. Part (i) is a straightforward two-step: nitrate toluene with mixed acid to install $-NO_2$ at p (with o as minor, easily separated) and then reduce with Fe/HCl (cheaper than Sn/HCl) to give p-toluidine. Part (ii) is a Sandmeyer-then-hydrolysis pair: replacing $-N_2{}^+$ by $-CN$ uses cuprous cyanide $CuCN$ in KCN; the resulting nitrile is then hydrolysed by hot aqueous acid all the way to the carboxylic acid, giving p-toluic acid. Each step is a standard textbook entry; the overall sequence builds a $-COOH$ at the same ring position where the original $-NH_2$ sat.

Final Answer: See answer above.

Q 9.60 Write following conversions:

(i) nitrobenzene $\rightarrow$ acetanilide; (ii) acetanilide $\rightarrow$ p-nitroaniline.

SOLUTION

Part (i): Nitrobenzene $\rightarrow$ acetanilide.

(a) Reduce nitrobenzene to aniline: $C_6H_5-NO_2 \xrightarrow{Sn\ /\ HCl} C_6H_5-NH_2$.

(b) Acylate aniline with acetic anhydride in pyridine:

$$C_6H_5-NH_2 + (CH_3CO)_2O \xrightarrow{pyridine} C_6H_5-NHCOCH_3 + CH_3COOH.$$

Part (ii): Acetanilide $\rightarrow$ p-nitroaniline.

(a) Nitrate with mixed acid:

$$C_6H_5-NHCOCH_3 \xrightarrow{HNO_3\ /\ H_2SO_4} p\text{-}O_2N-C_6H_4-NHCOCH_3.$$

(b) Acid hydrolysis:

$$p\text{-}O_2N-C_6H_4-NHCOCH_3 + H_2O \xrightarrow{H^+} p\text{-}O_2N-C_6H_4-NH_2 + CH_3COOH.$$

Concept used. Part (i) reduces nitrobenzene to aniline and acetylates. Part (ii) exploits acetanilide's o/p-directing $-NHCOCH_3$ to control nitration to the para position, then hydrolyses off the acetyl group.

> **Final Answer:** Sequences shown above. The protecting acetyl group is the trick that makes Part (ii) selective.

☞ Standard "protect-and-direct" move

Acylation tames the strongly activating $-NH_2$ so the ring survives nitration and points the new $-NO_2$ at the para position. Hydrolysis then unmasks $-NH_2$.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Protecting-group angle. Part (i) is a two-step preparation of acetanilide: reduce nitrobenzene to aniline with Sn/HCl (acidic dissolving metal), then acetylate the amine with acetic anhydride in pyridine (the pyridine soaks up the acetic acid by-product). Part (ii) needs p-nitroaniline, which cannot be made cleanly by direct nitration of aniline because the strong acid medium protonates the amine. The fix is to start from acetanilide (where the amine is already protected), nitrate with mixed acid to give predominantly the para-nitro product, and finally hydrolyse off the acetyl group to unmask p-nitroaniline. The acetyl protecting group is the unsung hero of the sequence.

> **Final Answer:** See sequences above.

Q 9.61 **A solution contains 1 g mol each of p-toluene diazonium chloride and p-nitrophenyl diazonium chloride. To this, 1 g mol of alkaline solution of phenol is added. Predict the major product. Explain your answer.**

SOLUTION

Major product: the azo dye coupling *p-nitrophenyl diazonium* with phenol, i.e. **4-nitro-4′-hydroxyazobenzene** $p\text{-}O_2N-C_6H_4-N=N-C_6H_4-OH^-p$, not the p-toluene version.

Concept used. **Azo coupling** is electrophilic aromatic substitution; rate scales with the electrophilicity of the diazonium cation. $-NO_2$ at the para position of the diazonium is strongly $-M/-I$ and *withdraws* electron density, making the diazonium more electrophilic. $-CH_3$ in the toluene-diazonium is mildly $+I$ and weakly donates, *lowering* the electrophilicity. So the nitro-substituted diazonium wins the race.

Step 1. Phenol in alkali $\rightarrow$ phenoxide (the nucleophile).

Step 2. Two competing electrophiles in solution: $p\text{-}O_2N-C_6H_4-N_2^+$ (more electrophilic) and $p\text{-}CH_3-C_6H_4-N_2^+$ (less electrophilic).

Step 3. Phenoxide couples preferentially with the stronger electrophile ⇒ p-nitrophenyldiazonium wins.

Step 4. Product: p-$O_2N-C_6H_4-N=N-C_6H_4-OH$, p-hydroxy-p'-nitroazobenzene (orange-red dye).

> **Final Answer:** Phenol preferentially couples with p-nitrophenyldiazonium chloride because $-NO_2$ raises the electrophilicity of the diazonium cation; product is 4-hydroxy-4′-nitroazobenzene.

☞ **Substituent rules for ArN2$^+$**

$-M/-I$ on the diazonium ring (e.g. $-NO_2$) → stronger electrophile → faster coupling. $+M/+I$ on the diazonium ring (e.g. $-CH_3$, $-OMe$) → weaker electrophile → slower coupling.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Electrophilicity-decides-the-race angle. Two aryl diazonium cations compete for one mole of phenoxide. Coupling is electrophilic aromatic substitution, so the diazonium that is more electrophilic wins. The p-nitrophenyldiazonium cation carries a strongly $-M/-I$ nitro group para to the $-N_2^+$, which sucks electron density out of the $-N=N-$ unit and concentrates positive charge there — making it a much hotter electrophile. The p-toluenediazonium has a mildly $+I$ methyl that donates a little density and softens the electrophile. So phenoxide couples preferentially with the nitro diazonium, giving 4-hydroxy-4′-nitroazobenzene as the major product.

> **Final Answer:** 4-Hydroxy-4′-nitroazobenzene (orange-red).

Q 9.62 How will you bring out the conversion: p-nitroaniline → 3,4,5-tribromonitrobenzene?

SOLUTION

Strategy. Use Br_2/CH_3COOH to brominate the ring of p-nitroaniline (the activating NH_2 directs Br to its two ortho positions, here both meta to the para-NO_2), then diazotise and remove the amine via H_3PO_2 to leave the three bromines on the ring.

(1) Bromination at both ortho positions to NH_2:

$$p\text{-}O_2N-C_6H_4-NH_2 + 2\,Br_2 \xrightarrow{CH_3COOH} 2,6\text{-dibromo-4-nitroaniline}$$

(the bromines sit at C-2 and C-6 of the aniline numbering, i.e. both ortho to NH_2

and meta to NO_2).

(2) Diazotisation at $0-5\,^\circ C$:

$$Ar{-}NH_2 + NaNO_2 + 2\,HCl \longrightarrow Ar{-}N_2^{+}\,Cl^{-} + 2\,H_2O$$

($Ar = 2,6\text{-}Br_2,{}_4\text{-}NO_2\text{-}C_6H_2$).

(3) Sandmeyer with Cu_2Br_2/HBr to install the third Br at the position vacated by $-N_2^{+}$:

$$Ar{-}N_2^{+}\,Cl^{-} + Cu_2Br_2 \longrightarrow Ar{-}Br + N_2 + CuCl + CuBr$$

giving 3,4,5-tribromonitrobenzene (positions $3,4,5$ when numbered from the nitro carbon: Br, Br, Br on C-3, C-4, C-5, NO_2 on C-1).

Final Answer: p-Nitroaniline $\xrightarrow{Br_2/CH_3COOH}$ 2,6-dibromo-4-nitroaniline $\xrightarrow{NaNO_2/HCl,\ 0\,^\circ C}$ diazonium $\xrightarrow{Cu_2Br_2/HBr}$ 3,4,5-tribromonitrobenzene.

☞ **Why two bromines first**

$-NH_2$ activates so strongly that two ortho positions brominate at once in acetic acid. The diazotisation/Sandmeyer step then installs the third Br where the amine was.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Three-step substitution angle. The conversion plants three bromines and removes the original amine. The first step exploits aniline's strong activation: in acetic acid, Br_2 attacks both ortho positions to the NH_2 (the para is blocked by NO_2). The second step locks the amine into the diazonium cation in the cold $0-5\,^\circ C$ window. The third step is a Sandmeyer in HBr/Cu_2Br_2 that swaps $-N_2^{+}$ for $-Br$, installing the final bromine at the original amine position. The product is the symmetrical 3,4,5-tribromonitrobenzene where the three bromines flank the para nitro group.

Final Answer: Three steps: Br_2/CH_3COOH, $NaNO_2/HCl$, Cu_2Br_2/HBr.

Q 9.63 How will you carry out the following conversion: benzene $\rightarrow$ p-nitroaniline?

SOLUTION

Strategy. Direct nitration of aniline gives mainly the meta product (because $-NH_3^{+}$ formed in strong acid is m-directing). We therefore (a) install nitro first, (b) reduce to

aniline, (c) protect $-NH_2$ as acetanilide so that the free pair on N is calmed and o/p is selective, (d) nitrate to get the p-acetamido-nitro arene, (e) hydrolyse back to $-NH_2$.

Step 1. Nitration of benzene with conc. HNO_3 and H_2SO_4:

$$C_6H_6 + HNO_3 \longrightarrow C_6H_5{-}NO_2 + H_2O$$

Step 2. Reduction of nitrobenzene with Sn and HCl:

$$C_6H_5{-}NO_2 + 6\,[H] \longrightarrow C_6H_5{-}NH_2 + 2\,H_2O$$

Step 3. Acetylation with acetic anhydride in pyridine (the $-NHCOCH_3$ group is still activating and p-directing, but no longer protonated by H_2SO_4):

$$C_6H_5{-}NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5{-}NHCOCH_3 + CH_3COOH$$

Step 4. Nitration of acetanilide with HNO_3/H_2SO_4 gives clean para selectivity:

$$C_6H_5{-}NHCOCH_3 + HNO_3 \longrightarrow \text{p-}NO_2{-}C_6H_4{-}NHCOCH_3 + H_2O$$

Step 5. Acid hydrolysis of the acetyl group with H_3O^+:

$$\text{p-}NO_2{-}C_6H_4{-}NHCOCH_3 + H_2O \longrightarrow \text{p-}NO_2{-}C_6H_4{-}NH_2 + CH_3COOH$$

> **Final Answer:** Benzene $\rightarrow$ nitrobenzene $\rightarrow$ aniline $\rightarrow$ acetanilide $\rightarrow$ p-nitroacetanilide $\rightarrow$ p-nitroaniline.

✗ Why protect with acetyl first?

Direct nitration of aniline gives *meta* (or oxidised tar) because the H_2SO_4 protonates $-NH_2$ to $-NH_3{}^+$, which is m-directing. Acetylation cools the ring; nitration then favours p.

EXPERT'S SOLUTION : *Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Five-step strategic angle. The conversion of benzene into p-nitroaniline is a five-move sequence in which the central trick is protecting the amine before the second nitration. *Move 1*: nitrate benzene with mixed acid to install $-NO_2$. *Move 2*: reduce nitrobenzene to aniline with Sn/HCl. *Move 3*: acetylate aniline with acetic anhydride in pyridine. This is the key step — the bulky, electron-withdrawing acetyl group caps the lone pair on nitrogen, preventing H_2SO_4 from protonating $-NH_2$ to the strongly m-directing $-NH_3{}^+$ that ruins direct nitration of free aniline.
Move 4: nitrate the acetanilide. Because $-NHCOCH_3$ is mildly activating and o/p-directing (with steric preference for para), NO_2 slots cleanly at the para position.

Move 5: hydrolyse the acetyl protecting group with aqueous acid to unmask the free amine, giving p-nitroaniline as the final product. Without the protect–deprotect dance, the second nitration would oxidise aniline and give mostly m-nitroaniline.

Final Answer: Five-step protect–deprotect sequence as above.

Q 9.64 How will you carry out the following conversion: aniline $\rightarrow$ m-bromonitrobenzene?

SOLUTION

Strategy. Diazotise the amine to $Ar{-}N_2^+$, install $-NO_2$ via Balz-Schiemann + radical pathway (but the standard NCERT key is even simpler): replace $-N_2^+$ by $-NO_2$ using Sandmeyer-like conditions with $NaNO_2/Cu$, then brominate at the now-activated meta position relative to $-NO_2$.

(1) Aniline + HNO_2 at $273-278\,K \rightarrow$ benzenediazonium chloride $C_6H_5{-}N_2^+\,Cl^-$.

(2) $C_6H_5{-}N_2^+\,Cl^- + HBF_4 \rightarrow C_6H_5{-}N_2^+\,BF_4^-$ (diazonium tetrafluoroborate, more stable for isolation).

(3) $C_6H_5{-}N_2^+\,BF_4^- + NaNO_2/Cu$, heat $\rightarrow C_6H_5{-}NO_2 + N_2$ (with copper by-products). NCERT route: $-N_2^+$ replaced by $-NO_2$.

(4) $C_6H_5{-}NO_2 + Br_2/FeBr_3 \rightarrow m$-$Br{-}C_6H_4{-}NO_2$. The $-NO_2$ is a strong m-director.

Concept used. Aniline cannot be directly nitrated at the meta position because $-NH_2$ (or $-NH_3^+$) does not direct that way usefully. Going via the diazonium and converting $-N_2^+$ to $-NO_2$ first removes the $-NH_2$ "label" entirely; then bromination of nitrobenzene installs $-Br$ at the meta position (since $-NO_2$ is m-directing).

Step 1. Step 1 & 2: convert $-NH_2$ to $-N_2^+\,BF_4^-$ for stability.

Step 2. Step 3: replace $-N_2^+$ by $-NO_2$ via $NaNO_2/Cu$.

Step 3. Step 4: bromination is directed by $-NO_2$ to meta $\Rightarrow$ m-bromonitrobenzene.

Final Answer: Aniline $\rightarrow C_6H_5N_2^+\,Cl^- \rightarrow C_6H_5N_2^+\,BF_4^- \rightarrow C_6H_5NO_2 \rightarrow$ m-bromonitrobenzene (via $Br_2/FeBr_3$).

☞ **Why not nitrate aniline directly?**

Direct nitration of aniline gives mostly tar (oxidation) or m-nitroaniline (from $-NH_3^+$); cannot give meta-bromonitrobenzene cleanly. The Sandmeyer-like detour is the textbook fix.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Detour-via-diazonium angle. Putting a $-\mathrm{Br}$ meta to a $-\mathrm{NO_2}$ on benzene is trivial once you have nitrobenzene ($-\mathrm{NO_2}$ is strongly m-directing). The challenge is to get nitrobenzene starting from aniline. Direct nitration of aniline fails for the reasons explored earlier (oxidation plus meta overrun from the protonated form). Instead, diazotise the amine to $-\mathrm{N_2}^+$ (stable at $0-5\,^\circ\mathrm{C}$), trap it as the more handleable tetrafluoroborate, and then use $\mathrm{NaNO_2/Cu}$ to swap $-\mathrm{N_2}^+$ for $-\mathrm{NO_2}$ giving nitrobenzene. Bromination of that nitrobenzene under $\mathrm{Br_2/FeBr_3}$ installs the meta bromine cleanly.

> **Final Answer:** Detour through the diazonium to nitrobenzene, then meta-brominate.

Q 9.65 **How will you carry out the following conversions?**

(i) Aniline $\rightarrow$ 3,5-dibromonitrobenzene.

(ii) Aniline $\rightarrow$ 3,5-dibromo-4-iodonitrobenzene (one extra I replacing the deaminated H of part (i)).

SOLUTION

Part (i): Aniline $\rightarrow$ 3,5-dibromonitrobenzene.

(a) Aniline $\xrightarrow{(\mathrm{CH_3CO})_2\mathrm{O}\,/\ \text{pyridine}}$ acetanilide.

(b) Acetanilide $\xrightarrow{\mathrm{HNO_3}\,/\,\mathrm{H_2SO_4}}$ p-nitroacetanilide.

(c) Acid hydrolysis: p-nitroacetanilide $\xrightarrow{\mathrm{H_3O^+}}$ p-nitroaniline.

(d) Bromination at the two ortho positions of $\mathrm{NH_2}$ (which are meta to $\mathrm{NO_2}$): p-nitroaniline $\xrightarrow{\mathrm{Br_2}\,/\,\mathrm{CH_3COOH}}$ 2,6-dibromo-4-nitroaniline.

(e) Diazotisation: 2,6-dibromo-4-nitroaniline $\xrightarrow{\mathrm{NaNO_2}\,/\,\mathrm{HCl},\ 273\text{-}278\ \mathrm{K}}$ diazonium chloride.

(f) Deamination with $\mathrm{H_3PO_2}$: $\xrightarrow{\mathrm{H_3PO_2}\,/\,\mathrm{H_2O}}$ 3,5-dibromonitrobenzene (the amine is replaced by $-\mathrm{H}$).

Part (ii): Aniline $\rightarrow$ 3,5-dibromo-4-iodonitrobenzene (one extra I relative to part (i)).

(a) Follow Part (i) steps (a)–(e) to get the 2,6-dibromo-4-nitrobenzenediazonium chloride.

(b) Replace $-\mathrm{N_2}^+$ by $-\mathrm{I}$ using KI (no Cu required): diazonium $\xrightarrow{\mathrm{KI}}$ 3,5-dibromo-4-iodonitrobenzene.

Concept used. The acetyl-protect-and-direct strategy installs $\mathrm{NO_2}$ at the para position. After deprotection, bromination installs two Br's at the ortho positions of $\mathrm{NH_2}$. The amine is then either deaminated (Part i) or replaced by iodide (Part ii) via the

diazonium.

> **Final Answer:** (i) Acylate → nitrate → hydrolyse → dibrominate → diazotise → H_3PO_2 deamination. (ii) Same first five steps; replace deamination with KI to install iodine.

☞ Aryl iodides need no Cu

$Ar{-}N_2^+ + KI \longrightarrow Ar{-}I$ at room temperature without copper, unlike chlorides/bromides (which need CuX, Sandmeyer) or fluorides (Balz-Schiemann).

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Multi-stage strategy angle. Both targets are 1,3,5-tri-substituted benzenes, which are hard to build by direct nitration/bromination because of competing directing effects. The solution exploits $-NH_2$ as a temporary directing group. Acetylate aniline, nitrate the acetanilide to install NO_2 at para, hydrolyse back to *p*-nitroaniline. Now the strongly activating $-NH_2$ sits para to $-NO_2$ and directs Br_2 to its two ortho positions, giving 2,6-dibromo-4-nitroaniline. Diazotise that amine, and the diazonium is either reduced to $-H$ with H_3PO_2 (Part i, giving 3,5-dibromonitrobenzene) or displaced by $-I$ with KI (Part ii, installing the fourth substituent as iodine).

> **Final Answer:** Six-step sequences in each part as listed above.

IV. Matching Type

Q 9.66 **Match the reactions given in Column I with the statements given in Column II.**

Column I	Column II
(i) Ammonolysis	(a) Amine with lesser number of carbon atoms
(ii) Gabriel phthalimide synthesis	(b) Detection test for primary amines
(iii) Hoffmann Bromamide reaction	(c) Reaction of phthalimide with KOH and R–X
(iv) Carbylamine reaction	(d) Reaction of alkyl halides with NH_3

SOLUTION

Matches: (i) → (d), (ii) → (c), (iii) → (a), (iv) → (b).
Concept used. Each named reaction has a single defining description.

Step 1. **Ammonolysis**: alkyl halide with ammonia,

$$\mathrm{R{-}X + NH_3 \longrightarrow R{-}NH_2 + HX}$$

(over-alkylates to give $1^\circ/2^\circ/3^\circ/4^\circ$ mix) $\Rightarrow$ matches (d).

Step 2. **Gabriel synthesis**: phthalimide + KOH gives $\mathrm{Phth{-}N^-\,K^+}$, then + R–X and hydrolysis $\Rightarrow$ matches (c).

Step 3. **Hoffmann bromamide**: a primary amide reacts with bromine in aqueous NaOH to give a one-carbon-shorter primary amine,

$$\mathrm{R{-}CONH_2 + Br_2 + 4\,NaOH \longrightarrow R{-}NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O}$$

$\Rightarrow$ matches (a).

Step 4. **Carbylamine test**: 1° amine + $\mathrm{CHCl_3}$ + KOH → R–NC (foul-smelling isocyanide) — positive only for 1° amines $\Rightarrow$ matches (b).

Final Answer: (i)→(d), (ii)→(c), (iii)→(a), (iv)→(b).

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

One-keyword angle. Match each named reaction to its single most defining keyword in Column II. "Alkyl halide plus $\mathrm{NH_3}$" is the literal definition of ammonolysis, so (i)→(d). "Phthalimide with KOH and R–X" is the literal Gabriel recipe, so (ii)→(c). "Amine with fewer carbon atoms" is the headline feature of the Hoffmann bromamide degradation (loses one carbon as $\mathrm{Na_2CO_3}$), so (iii)→(a). "Detection test for primary amines" — the obnoxious isocyanide smell from $\mathrm{CHCl_3/KOH}$ — nails the carbylamine test, so (iv)→(b).

Final Answer: (i)→(d), (ii)→(c), (iii)→(a), (iv)→(b).

Q 9.67 **Match the compounds given in Column I with the items given in Column II.**

Column I	Column II
(i) Benzene sulphonyl chloride	(a) Zwitter ion
(ii) Sulphanilic acid (p-aminobenzenesulphonic acid)	(b) Hinsberg reagent
(iii) Alkyl diazonium salts	(c) Dyes
(iv) Aryl diazonium salts	(d) Conversion to alcohols

SOLUTION

Matches: (i) $\rightarrow$ (b), (ii) $\rightarrow$ (a), (iii) $\rightarrow$ (d), (iv) $\rightarrow$ (c).
Concept used. Each compound has a single signature property in the list.

Step 1. **Benzenesulphonyl chloride** ($C_6H_5SO_2Cl$) is the literal Hinsberg reagent $\Rightarrow$ matches (b).

Step 2. **Sulphanilic acid** $H_2N{-}C_6H_4{-}SO_3H$ exists in a zwitterionic tautomer $H_3N^+{-}C_6H_4{-}SO_3^-$ where the protonated amine balances the deprotonated sulphonate. This zwitterion is responsible for its high mp ($\sim 288\,^\circ C$) and insolubility in non-polar solvents $\Rightarrow$ matches (a).

Step 3. **Alkyl diazonium salts** $R{-}N_2^+$ decompose at once (because the cation is not aromatic-stabilised), giving alcohols on water trapping $\Rightarrow$ matches (d).

Step 4. **Aryl diazonium salts** $Ar{-}N_2^+$ are stable at $0 - 5\,^\circ C$ and undergo azo coupling with activated arenes (phenol, aniline) to give azo dyes (orange/red) $\Rightarrow$ matches (c).

Final Answer: (i)$\rightarrow$(b), (ii)$\rightarrow$(a), (iii)$\rightarrow$(d), (iv)$\rightarrow$(c).

☞ **Zwitterion of sulphanilic acid**

Free aniline + free $-SO_3H$ would be unstable in proximity. The intramolecular acid-base proton transfer gives the zwitterion, which is the stable form.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Single-keyword-match angle. Each Column I entry has one defining downstream behaviour. Benzenesulphonyl chloride is the literal Hinsberg reagent used to distinguish $1^\circ/2^\circ/3^\circ$ amines, mapping cleanly to entry (b). Sulphanilic acid exists as a zwitterion ($H_3N^+{-}C_6H_4{-}SO_3^-$) because the molecule contains both a basic amine and an acidic sulphonate; this is what gives it its unusually high melting point and water solubility, mapping to (a). Alkyl diazonium salts are intrinsically unstable, fragment on formation, and give alcohols when water traps the carbocation ($\rightarrow$ (d)). Aryl diazonium salts are stable below $5\,^\circ C$, undergo azo coupling with activated arenes (phenol, aniline), and the

resulting azo compounds historically launched the synthetic dye industry — mapping to (c).

> **Final Answer:** (i)→(b), (ii)→(a), (iii)→(d), (iv)→(c).

V. Assertion and Reason Type

> ☞ **Note**
> (i) Both A & R wrong. (ii) Both correct, R *not* the correct explanation. (iii) A correct, R wrong. (iv) Both correct & R is the correct explanation. (v) A wrong but R correct.

Q 9.68 **Assertion (A): Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.**
Reason (R): Acyl group sterically hinders the approach of further acyl groups.

SOLUTION

Correct option: (iii) A is correct, R is wrong.
Concept used. Acylation of an amine stops at the monosubstituted product because the freshly formed amide nitrogen $\mathrm{R{-}NH{-}CO{-}R_2}$ is much *less nucleophilic* than the starting amine (the carbonyl drains N via $-M$). Steric hindrance is a minor factor at best. The textbook reason is electronic, not steric.

Step 1. Alkylation: $\mathrm{R{-}NH_2 + R_2{-}X \longrightarrow R{-}NH{-}R_2}$, then $\mathrm{R{-}NH{-}R_2}$ is even more nucleophilic than $\mathrm{R{-}NH_2}$ (extra $+I$) $\Rightarrow$ second alkylation runs faster $\Rightarrow$ polysubstitution.

Step 2. Acylation: $\mathrm{R{-}NH_2 + R_2{-}COX \longrightarrow R{-}NH{-}CO{-}R_2}$, then $\mathrm{R{-}NH{-}CO{-}R_2}$ has its lone pair tied up in amide resonance $\Rightarrow$ much less nucleophilic $\Rightarrow$ second acylation is slow.

Step 3. Reason as stated cites steric hindrance only — this is not the dominant factor; the dominant factor is the loss of nucleophilicity.

> **Final Answer:** Option **(iii)** — assertion correct, reason wrong (the reason is electronic, not steric).

> ☞ **The amide nitrogen is barely nucleophilic**
> Amide nitrogen is the least basic/least nucleophilic nitrogen in common organic chemistry ($\mathrm{p}K_b \approx 14$), thanks to extensive lone-pair delocalisation into the carbonyl. That is why acylation self-terminates.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Electronic-vs-steric angle. Evaluate the two statements separately. The assertion is straightforwardly correct: in practice acylation of an amine stops cleanly at one substitution, while alkylation gives a mix of all four substitution products ($1^\circ/2^\circ/3^\circ/4^\circ$). The reason attributes that selectivity to steric hindrance from the first acyl group. That mechanism is not the dominant cause — the real cause is electronic. Once the first acyl group is installed, the amide nitrogen's lone pair is delocalised into the carbonyl, so nitrogen is no longer a competent nucleophile. The next acylation is therefore electronically suppressed, not sterically blocked. A correct, R incorrect $\Rightarrow$ option (iii).

Final Answer: Option **(iii)**.

Q 9.69 **Assertion (A): Hoffmann's bromamide reaction is given by primary amines. Reason (R): Primary amines are more basic than secondary amines.**

SOLUTION

Correct option: (iii) — A is correct, but R is wrong.

Concept used. **Hoffmann bromamide** converts a 1° *amide* ($\mathrm{R{-}CONH_2}$) to a 1° *amine* ($\mathrm{R{-}NH_2}$) by treatment with $\mathrm{Br_2/NaOH}$ — the substrate is an amide, not an amine. The assertion as worded is acceptable in the NCERT key ("given by primary amines" here means the product is a 1° amine; one-carbon shorter). The reason is factually wrong: in aqueous medium $2^\circ > 1^\circ$ in basicity.

Step 1. Hoffmann:
$$\mathrm{R{-}CONH_2 + Br_2 + 4\,NaOH \longrightarrow R{-}NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O}.$$

Step 2. Mechanism: N-bromination, deprotonation, α-elimination to isocyanate $\mathrm{R{-}N{=}C{=}O}$, hydrolysis to amine. Only $\mathrm{R{-}CONH_2}$ (not the N-substituted amide $\mathrm{R{-}CONHR}$) has the two acidic N–H needed.

Step 3. R: aqueous basicity is $2^\circ > 1^\circ \approx 3^\circ$ — the reason is false.

Final Answer: Option **(iii)** — assertion correct (per NCERT key), reason incorrect.

☞ **NCERT phrasing nit-pick**

"Given by primary amines" is loose — the substrate is the 1° *amide*, the product is the 1° amine. The NCERT answer key still marks A as correct.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Two-statement angle. Evaluate Assertion and Reason independently before mapping to the five options.

Assertion. "Hoffmann's bromamide reaction is given by primary amines" is the standard NCERT phrasing, where "given by" means the product is a primary amine; the substrate is the primary amide $\mathrm{R{-}CONH_2}$, the reagent is $\mathrm{Br_2/NaOH}$, and the amine obtained has one fewer carbon than the starting amide. The reaction proceeds via N-bromination, deprotonation, nitrene formation, alkyl migration to an isocyanate, and final hydrolysis to $\mathrm{R{-}NH_2}$. So A is correct as accepted by NCERT.

Reason. "Primary amines are more basic than secondary amines" is wrong for aqueous medium, where the well-known order is $2^\circ > 1^\circ \approx 3^\circ > \mathrm{NH_3}$. It is also unrelated to Hoffmann bromamide, which depends on amide N–H acidity, not amine basicity. Hence R is false.

A correct + R wrong maps to option (iii).

Final Answer: Option **(iii)**: A correct, R incorrect.

Q 9.70 **Assertion (A): N-Ethylbenzenesulphonamide is soluble in alkali.**
Reason (R): Hydrogen attached to nitrogen in sulphonamide is strongly acidic.

SOLUTION

Correct option: (iv) both correct; R correctly explains A.

Concept used. N-ethylbenzenesulphonamide is $\mathrm{C_6H_5{-}SO_2{-}NH{-}C_2H_5}$ — the Hinsberg product from a 1° amine ($\mathrm{EtNH_2}$). The remaining $\mathrm{N{-}H}$ is rendered acidic by the two strongly electron-withdrawing $\mathrm{S{=}O}$ groups, so NaOH deprotonates it to a soluble sodium salt $\mathrm{C_6H_5{-}SO_2{-}N^-\,C_2H_5\;Na^+}$.

Step 1. Resonance: $\mathrm{R{-}SO_2{-}N^-{-}R_2 \longleftrightarrow R{-}S(=O)(-O^-){-}N{-}R_2}$ stabilises the conjugate base by delocalisation of the negative charge onto the sulphonyl oxygens.

Step 2. $\mathrm{p}K_a$ of sulphonamide $\mathrm{N{-}H}$ is ~ 10 (a weak acid, comparable to phenol), low enough for NaOH to deprotonate.

Step 3. Sodium salt is ionic $\Rightarrow$ water-soluble.

Final Answer: Option **(iv)**: A correct, R correct, R explains A.

☞ **Hinsberg solubility behaviour**

This is exactly the diagnostic for a 1° amine in the Hinsberg test: a 1° amine $\rightarrow$ Hinsberg sulphonamide that dissolves in NaOH (acidic $\mathrm{N{-}H}$); 2° amine $\rightarrow$ Hinsberg sulphonamide with no $\mathrm{N{-}H}$, NaOH-insoluble; 3° amine $\rightarrow$ no reaction.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Acidic N–H angle. N-ethylbenzenesulphonamide is the product of treating a primary amine ($\mathrm{EtNH_2}$) with Hinsberg reagent. The nitrogen still bears one $\mathrm{N{-}H}$, which is rendered acidic ($\mathrm{p}K_a \approx 10$) by the electron-pulling $\mathrm{S{=}O}$ groups: deprotonation gives a sulphonamide anion in which the negative charge is spread over the two sulphonyl oxygens by resonance. That conjugate-base stabilisation lets dilute NaOH deprotonate the $\mathrm{N{-}H}$ and dissolve the sulphonamide as a sodium salt. So the assertion (the sulphonamide dissolves in alkali) and the reason (the $\mathrm{N{-}H}$ is strongly acidic) are both correct, and the reason is the direct cause of the assertion.

Final Answer: Option **(iv)**.

Q 9.71 **Assertion (A): N,N-Diethylbenzenesulphonamide is insoluble in alkali. Reason (R): Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.**

SOLUTION

Correct option: (ii) both correct, but R is *not* the correct explanation of A.

Concept used. N,N-Diethylbenzenesulphonamide $\mathrm{C_6H_5{-}SO_2{-}N(Et)_2}$ comes from a 2° amine ($\mathrm{Et_2NH}$). The nitrogen has *no* $\mathrm{N{-}H}$ to lose, so NaOH has nothing to deprotonate and the sulphonamide stays insoluble in alkali. The fact that the sulphonyl group is electron-withdrawing is true, but that property would only matter if there were an $\mathrm{N{-}H}$ to acidify; since there isn't, that "reason" is real but irrelevant to the insolubility.

Step 1. Structure: $\mathrm{C_6H_5{-}SO_2{-}N(C_2H_5)_2}$ — two ethyls on N, no $\mathrm{N{-}H}$.

Step 2. In NaOH: no acidic proton to remove $\Rightarrow$ no salt formation $\Rightarrow$ insoluble.

Step 3. R is a true statement (sulphonyl group is indeed EW), but it does not explain why this particular sulphonamide is insoluble. The actual cause is the *absence* of $\mathrm{N{-}H}$.

Final Answer: Option **(ii)**: A correct, R correct (true statement), but R does *not* explain A.

☞ **Both correct, but unrelated**

Watch out for the "(ii)" option in A-R type: both statements may be true but unrelated. The reason here is a true chemistry fact, but the actual cause of insolubility is the lack of an $N-H$, not the EW nature of $-SO_2-$.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Distinct-correct-statements angle. N,N-Diethylbenzenesulphonamide arises from a secondary amine (Et_2NH) reacting with Hinsberg reagent. The nitrogen carries two ethyl groups and zero hydrogens, so there is simply no $N-H$ for sodium hydroxide to deprotonate; the sulphonamide remains as a neutral, alkali-insoluble solid. The reason, that $-SO_2-$ is a strong electron-withdrawing group, is itself a true statement of chemistry, but it only matters when an $N-H$ exists to be acidified. Here it does not. So the assertion and reason are individually correct but the reason is not the cause of the assertion — option (ii).

Final Answer: Option **(ii)**.

Q 9.72 **Assertion (A): Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.**
Reason (R): $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.

SOLUTION

Correct option: (iv) both correct; R correctly explains A.
Concept used. In the industrial Bechamp reduction ($Ar-NO_2 \longrightarrow Ar-NH_2$) with Fe scrap, HCl and steam, HCl is effectively *catalytic*: the $FeCl_2$ formed in the reduction hydrolyses with steam to give back HCl and $Fe(OH)_2$. So only a small starting charge of HCl is needed — it keeps getting regenerated.

Step 1. Reduction: $Ar-NO_2 + 3\,Fe + 6\,HCl \longrightarrow Ar-NH_2 + 3\,FeCl_2 + 2\,H_2O$.

Step 2. Hydrolysis: $FeCl_2 + 2\,H_2O \longrightarrow Fe(OH)_2 + 2\,HCl\uparrow$ (steam-assisted).

Step 3. Net effect: HCl from step 1 is regenerated in step 2 $\Rightarrow$ HCl is catalytic, not stoichiometric.

Final Answer: Option **(iv)**: A correct, R correct, R explains A. HCl is effectively catalytic via $FeCl_2$ hydrolysis.

♥ Industrial economy

This is exactly why Fe/HCl beats Sn/HCl at plant scale: iron is cheap and HCl can be used catalytically. Sn/HCl needs stoichiometric HCl and Sn is expensive.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Catalytic-acid angle. The Bechamp reduction of an aromatic nitro compound to the amine consumes HCl when iron metal donates electrons to $-NO_2$. The HCl is needed to protonate the intermediates and pull them through to $Ar-NH_3^+\ Cl^-$. But the $FeCl_2$ that the same reaction produces is a Lewis-acidic salt that hydrolyses readily, especially in the presence of steam, to give back HCl and $Fe(OH)_2$. The HCl liberated from hydrolysis re-enters the reaction. The net effect is that only a small starting charge of HCl is needed to keep the reduction running, exactly as the assertion states. Both statements are correct and the reason cleanly explains the assertion — option (iv).

Final Answer: Option **(iv)**.

Q 9.73 **Assertion (A): Aromatic 1° amines can be prepared by Gabriel Phthalimide Synthesis.**
Reason (R): Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.

SOLUTION

Correct option: (i) both A and R are wrong.
Concept used. Gabriel synthesis fails for aromatic amines because aryl halides ($Ar-X$) do not undergo S_N2 (the sp^2 carbon has no backside lobe; the ring π system blocks attack). So:

- Assertion is wrong — aromatic 1° amines (e.g. aniline) cannot be prepared by Gabriel.
- Reason is wrong — aryl halides do *not* undergo S_N2 with phthalimide anion (or with most nucleophiles), they only undergo nucleophilic aromatic substitution under specific activating conditions (strong EW groups on the ring), which is not relevant here.

Step 1. Gabriel substrate scope: 1° and 2° *alkyl* halides only.

Step 2. Aryl halide C_6H_5-X + phthalimide anion $\rightarrow$ no reaction.

Step 3. Aniline is therefore made by other routes (e.g. reduction of nitrobenzene).

Final Answer: Option **(i)** — both A and R are wrong. Gabriel cannot make aromatic amines because aryl halides don't S_N2.

✗ Gabriel's substrate scope

Memorise: Gabriel is for 1° alkyl halides $\rightarrow$ 1° alkyl amines. "Aryl" and "$2^\circ/3^\circ$ amine targets" are both forbidden.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Substrate-scope angle. The Gabriel synthesis only works when the alkyl halide can undergo backside S_N2 on the phthalimide nitrogen. Aryl halides do not do S_N2 because their sp^2 carbon does not present a backside lobe for attack, and the ring π system electronically shields the carbon. So aniline cannot be made by Gabriel synthesis; the NCERT route to aniline is reduction of nitrobenzene with Sn/HCl or Fe/HCl. Both the assertion (Gabriel can make aromatic amines) and the reason (aryl halides undergo S_N2 with phthalimide anion) are wrong, so the answer is option (i).

Final Answer: Option **(i)**.

Q 9.74 **Assertion (A): Acetanilide is less basic than aniline.**
Reason (R): Acetylation of aniline results in decrease of electron density on nitrogen.

SOLUTION

Correct option: (iv) — both correct, and R correctly explains A.
Concept used. Basicity of an amine tracks electron density on N. Acetylation converts $Ar{-}NH_2$ (aniline) to $Ar{-}NH{-}COCH_3$ (acetanilide). The acetyl carbonyl is a strong π-acceptor: the N lone pair delocalises onto the carbonyl O ($N{-}C{=}O \leftrightarrow N^+{=}C{-}O^-$). Density on N drops $\Rightarrow$ basicity drops.

Step 1. Aniline $pK_b \approx 9.4$ (i.e. a weak base).

Step 2. Acetanilide $pK_b \approx 13.6$ — about 4 orders of magnitude weaker.

Step 3. Cause: the amide resonance $-NH{-}CO{-}CH_3 \leftrightarrow -NH^+{=}C(O^-){-}CH_3$ drains the lone pair from N onto O.

Final Answer: Option **(iv)** — A correct, R correct, R explains A.

☞ Why we acetylate before nitration

This same drop in N density is the reason acetylation tames aniline before nitration — it stops oxidation and prevents the strongly m-directing $-NH_3^+$ form.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Resonance-loss angle. Aniline already pays a basicity penalty because its N lone pair partially delocalises into the benzene ring ($pK_b \approx 9.4$). Acetylation deepens this loss — the nitrogen lone pair now also has the strongly π-accepting amide carbonyl to delocalise into, producing the resonance structure $R{-}N^+{=}C(O^-){-}CH_3$. That second delocalisation pulls density off N to the extent that acetanilide ($pK_b \approx 13.6$) is about four orders of magnitude weaker as a base than aniline.
The assertion (acetanilide less basic than aniline) and the reason (acetylation lowers electron density on N) are both correct, and the reason is the direct mechanistic explanation of the assertion. That fixes option (iv) as the answer key.

Final Answer: Option **(iv)** — both correct, R explains A.

VI. Long Answer Type

Q 9.75 **A hydrocarbon 'A' (C_4H_8) on reaction with HCl gives a compound 'B' (C_4H_9Cl), which on reaction with 1 mol of NH_3 gives compound 'C' ($C_4H_{11}N$). On reacting with $NaNO_2$ and HCl followed by treatment with water, compound 'C' yields an optically active alcohol, 'D'. Ozonolysis of 'A' gives 2 mols of acetaldehyde. Identify compounds 'A' to 'D'.**

SOLUTION

Concept used. Three diagnostic clues pin down each species: (1) ozonolysis of an alkene to two carbonyls fixes the *position of the double bond*; (2) Markovnikov addition of HCl converts an alkene into the more-substituted alkyl halide; (3) reaction with $NaNO_2$/HCl followed by water on a 1° aliphatic amine gives the corresponding alcohol via a short-lived diazonium ion.

Step 1. Ozonolysis of A $\rightarrow$ 2 mol CH_3CHO. Hence A is symmetrical with a C=C between two $CH{-}CH_3$ units.

Step 2. Therefore A = but-2-ene, $CH_3{-}CH{=}CH{-}CH_3$.

Step 3. A + HCl: Markovnikov on a symmetrical alkene gives B = $CH_3{-}CHCl{-}CH_2{-}CH_3$, 2-chlorobutane.

Step 4. $B + NH_3$ (1 mol): S_N2 at the 2° centre gives $C = CH_3{-}CH(NH_2){-}CH_2{-}CH_3$, butan-2-amine (a 1° amine on a chiral sp^3 carbon).

Step 5. $C + NaNO_2/HCl + H_2O$: diazonium decomposes; water traps the cation with mostly retained configuration $\Rightarrow$ $D = CH_3{-}CH(OH){-}CH_2{-}CH_3$, butan-2-ol — optically active (chiral C).

A: $CH_3{-}CH{=}CH{-}CH_3$ (but-2-ene)

$\downarrow$ + HCl (Markovnikov)

B: $CH_3{-}CHCl{-}CH_2CH_3$ (2-chlorobutane)

$\downarrow$ + NH_3

C: $CH_3{-}CH(NH_2){-}CH_2CH_3$ (butan-2-amine)

$\downarrow$ $NaNO_2/HCl$, then H_2O

D: $CH_3{-}CH(OH){-}CH_2CH_3$ (s-butanol, optically active)

Final Answer: A = but-2-ene; B = 2-chlorobutane; C = butan-2-amine; D = butan-2-ol (chiral, optically active).

☞ Why the alcohol is optically active

Both B and C already contain the chiral C-2. As long as a chiral synthesis (e.g. starting from (R)-2-chlorobutane) is implied, the alcohol D retains chirality. The NCERT key takes the chiral centre at face value.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Backward-from-ozonolysis angle. The cleanest entry point is the ozonolysis clue. Two molecules of acetaldehyde imply that the parent alkene A is symmetrical with a C=C bond between two $CH{-}CH_3$ units. Splice the two acetaldehyde carbonyls together and you reach $A = CH_3{-}CH{=}CH{-}CH_3$, i.e. but-2-ene with formula C_4H_8.
The downstream cascade is then automatic. Markovnikov addition of HCl to a symmetric alkene gives B, 2-chlorobutane $CH_3{-}CHCl{-}CH_2CH_3$ (a 2° alkyl chloride). One mole of NH_3 does S_N2 at that 2° centre to give C, butan-2-amine $CH_3{-}CH(NH_2){-}CH_2CH_3$ — a primary amine on a chiral carbon. Treating C with $NaNO_2/HCl$ generates an aliphatic diazonium intermediate that loses N_2 rapidly; water

captures the resulting secondary carbocation to give D, butan-2-ol $CH_3{-}CH(OH){-}CH_2CH_3$. Because the chiral C-2 carries through every step, the final alcohol D is optically active (an R/S centre that the NCERT key counts as a single enantiomer).

> **Final Answer:** A = but-2-ene, B = 2-chlorobutane, C = butan-2-amine, D = butan-2-ol (optically active).

Q 9.76 **A colourless substance 'A' (C_6H_7N) is sparingly soluble in water and gives a water-soluble compound 'B' on treating with mineral acid. On reacting with $CHCl_3$ and alcoholic potash 'A' produces an obnoxious smell due to the formation of compound 'C'. Reaction of 'A' with benzenesulphonyl chloride gives compound 'D' which is soluble in alkali. With $NaNO_2$ and HCl, 'A' forms compound 'E' which reacts with phenol in alkaline medium to give an orange dye 'F'. Identify compounds 'A' to 'F'.**

SOLUTION

Concept used. Six classical aniline tests — (a) basicity (soluble in mineral acid), (b) carbylamine test ($CHCl_3/KOH$ on 1° amine), (c) Hinsberg (1° amine gives alkali-soluble sulphonamide), (d) diazotisation at $0-5\,^\circ C$, (e) coupling of $Ar{-}N_2{}^+$ with phenol in alkali to give an orange dye — all fit aniline.

Step 1. Formula C_6H_7N, sparingly water-soluble colourless liquid: **aniline**, $C_6H_5{-}NH_2$. Hence $A = C_6H_5NH_2$.

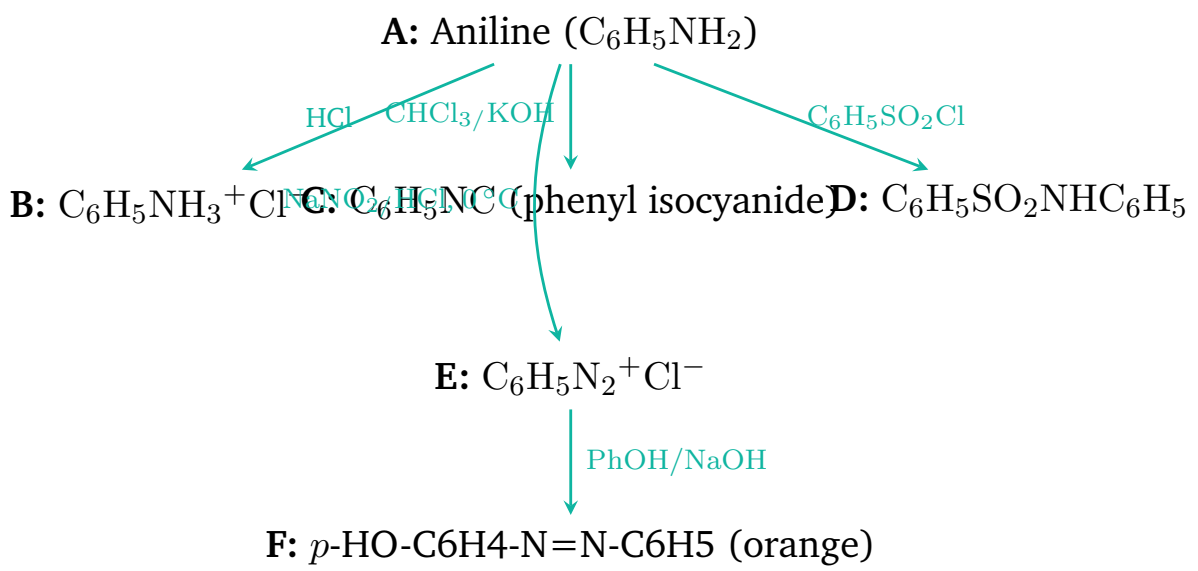
Step 2. $A + HCl \longrightarrow C_6H_5NH_3{}^+\,Cl^-$, a salt soluble in water. B = anilinium chloride.

Step 3. On heating, $A + CHCl_3 + 3\ KOH \longrightarrow C_6H_5{-}NC + 3\,KCl + 3\,H_2O$ (the obnoxious smell). C = phenyl isocyanide C_6H_5NC.

Step 4. $A + C_6H_5SO_2Cl \longrightarrow C_6H_5{-}SO_2{-}NH{-}C_6H_5 + HCl$, where the remaining $N{-}H$ is acidic and dissolves in NaOH. $D = N$-phenylbenzenesulphonamide.

Step 5. $A + NaNO_2/HCl$ at $0-5\,^\circ C \rightarrow C_6H_5{-}N_2{}^+\,Cl^-$. E = benzene diazonium chloride.

Step 6. $E + C_6H_5OH/NaOH$ at $0\,^\circ C \rightarrow C_6H_5{-}N{=}N{-}C_6H_4{-}OH$ (para). $F = p$-hydroxyazobenzene (orange dye).



Final Answer: A = aniline, B = anilinium chloride, C = phenyl isocyanide, D = *N*-phenylbenzenesulphonamide, E = benzenediazonium chloride, F = *p*-hydroxyazobenzene.

✗ Coupling needs mild alkali

Coupling of ArN_2^+ with phenol is done at $0-5\,^\circ C$ in dilute NaOH (the more reactive phenoxide), *not* in strong base (which would destroy the diazonium salt).

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Identify-A-then-cascade angle. The opening clues do most of the work. A neutral C_6H_7N compound that is colourless, sparingly water-soluble, but dissolves in mineral acid can only be a weak basic amine; given the carbon count, the only realistic candidate is aniline $C_6H_5-NH_2$. Once A is locked, the remaining transformations are a clean tour of the five canonical aniline reactions.

B is the protonated salt $C_6H_5-NH_3^+\,Cl^-$, water-soluble by virtue of being ionic. *C* comes from the carbylamine test: chloroform plus KOH on a 1° amine gives phenyl isocyanide C_6H_5-NC, notorious for its obnoxious smell — the classroom fingerprint of an aniline-class amine. *D* is the Hinsberg sulphonamide $C_6H_5-SO_2-NH-C_6H_5$, alkali-soluble because the remaining $N-H$ is acidified by the sulphonyl.

E is benzenediazonium chloride $C_6H_5-N_2^+\,Cl^-$, made stable by aryl resonance at $0-5\,^\circ C$. Finally *F* is the azo dye that comes from coupling the diazonium with phenol in alkaline medium: the phenoxide is the nucleophile, attack at para gives *p*-hydroxyazobenzene, an orange dye that historically launched the synthetic dye industry. Every step is a one-line entry in the standard aniline reagent table.

Final Answer: A = aniline, B = anilinium chloride, C = phenyl isocyanide, D = N-phenylbenzenesulphonamide, E = benzenediazonium chloride, F = p-hydroxyazobenzene.

Q 9.77 **Predict the reagent or the product in the following reaction sequence (NCERT Exemplar Q77):**

$$p\text{-nitrotoluene} \xrightarrow{1} p\text{-toluidine} \xrightarrow{(CH_3CO)_2O\ /\ \text{pyridine}} p\text{-methylacetanilide}$$
$$\xrightarrow{HNO_3\ /\ H_2SO_4} 2 \xrightarrow{3} 4'\text{-methyl-}2'\text{-nitroaniline}$$
$$\xrightarrow{NaNO_2\ /\ HCl} 4 \xrightarrow{5} m\text{-nitrotoluene}.$$

Identify the reagents and intermediates labelled $1, 2, 3, 4, 5$.

SOLUTION

Answers

- **1 (reagent)**: $Sn\ /\ HCl$ (or $Fe\ /\ HCl$) — reduction of $Ar{-}NO_2$ to $Ar{-}NH_2$.
- **2 (intermediate)**: 4-methyl-2-nitroacetanilide (a benzene ring with CH_3 at C-4, $NHCOCH_3$ at C-1, and NO_2 at C-2; i.e. NO_2 goes ortho to the $NHCOCH_3$ since para is blocked by CH_3).
- **3 (reagent)**: H_3O^+ (or $H^+\ /\ H_2O,\ \Delta$) — acid hydrolysis to remove the acetyl group, giving 4-methyl-2-nitroaniline.
- **4 (intermediate)**: 4-methyl-2-nitrobenzenediazonium chloride $4\text{-}CH_3\text{-}2\text{-}NO_2\text{-}C_6H_3\text{-}N_2^+\ Cl^-$.
- **5 (reagent)**: $H_3PO_2\ /\ H_2O$ (hypophosphorous acid) — deamination: replaces $-N_2^+$ by $-H$, giving m-nitrotoluene.

Concept used. The route uses (a) Sn/HCl reduction to unlock the amine from p-nitrotoluene, (b) acetyl protection of the amine before nitration, (c) ortho-directed nitration of the acetamido-arene, (d) acid hydrolysis to free the amine, (e) diazotisation and (f) H_3PO_2 deamination to put a hydrogen where the amine was. The product is m-nitrotoluene (NO_2 at C-3 of toluene), where NO_2 and CH_3 sit *meta* to each other — a regiochemistry unreachable by direct nitration of toluene.

Step 1. Step 1: p-nitrotoluene $\xrightarrow{Sn\ /\ HCl}$ p-toluidine.

Step 2. Step 2: p-toluidine + $(CH_3CO)_2O$/pyridine $\rightarrow$ p-methylacetanilide (the amine is protected as acetamide).

Step 3. Step 3 (intermediate 2): nitration with HNO_3/H_2SO_4. Since para to the $NHCOCH_3$ is blocked by CH_3, NO_2 enters *ortho* to the $NHCOCH_3$ $\Rightarrow$

4-methyl-2-nitroacetanilide.

Step 4. Step 4 (reagent 3): acid hydrolysis H_3O^+ removes acetyl $\rightarrow$ 4-methyl-2-nitroaniline.

Step 5. Step 5 (intermediate 4): diazotisation with $NaNO_2/HCl$ at $0-5\,^\circ C \rightarrow$ diazonium chloride.

Step 6. Step 6 (reagent 5): H_3PO_2/H_2O deaminates $-N_2^+ \longrightarrow -H \rightarrow m$-nitrotoluene.

Final Answer: 1 = Sn/HCl; 2 = 4-methyl-2-nitroacetanilide; 3 = H_3O^+ hydrolysis; 4 = 4-methyl-2-nitrobenzenediazonium chloride; 5 = H_3PO_2/H_2O.

☞ **The whole point of this synthesis**

m-nitrotoluene cannot be made by direct nitration of toluene (which gives o/p). The route uses $-NH_2$ as a temporary directing group: it steers NO_2 to the right position, then is removed by deamination.

EXPERT'S SOLUTION *: Priya Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Use-the-amine-then-remove-it angle. Direct nitration of toluene gives only the o- and p-nitrotoluenes because $-CH_3$ is an o/p-director. To install $-NO_2$ at the meta position, the sequence introduces a temporary $-NH_2$ at C-1 (via reduction of p-nitrotoluene), protects it as the acetamide, nitrates — which puts NO_2 ortho to the acetamide because para is blocked by CH_3 — hydrolyses off the acetyl, diazotises the amine, and finally deaminates with hypophosphorous acid to replace the amine with a hydrogen. The result is m-nitrotoluene, a substitution pattern impossible to reach without the amine positioning trick. The five blanks correspond to (1) Sn/HCl, (2) 4-methyl-2-nitroacetanilide, (3) H_3O^+ hydrolysis, (4) the diazonium chloride, (5) H_3PO_2/H_2O deamination.

Final Answer: See itemised answers above.

Chapter at a glance

- **Classes:** count C atoms on N: 1, 2, 3 $\Rightarrow 1^\circ, 2^\circ, 3^\circ$. "$tert$-butyl" on N is still 1°.
- **Basicity (water):** $2^\circ > 1^\circ \approx 3^\circ > NH_3 >$ aryl amine; EDG on ring helps, EWG ($-NO_2$) hurts.
- **Gabriel:** $Phth{-}N^- + R{-}X \longrightarrow R{-}NH_2$. Pure 1° amines from $1^\circ/2^\circ$ alkyl halides only; fails for aryl.
- **Hoffmann bromamide:** $R{-}CONH_2$ with Br_2 and NaOH gives $R{-}NH_2$; drops one carbon.

- **Reduce** $\mathrm{Ar{-}NO_2}$**:** Sn/HCl, Fe/HCl, $\mathrm{H_2}$/cat.; avoid $\mathrm{LiAlH_4}$ (gives azo).
- **Diazotisation:** aryl $\mathrm{NaNO_2/HCl}$ at $0-5\,^\circ\mathrm{C} \rightarrow$ stable $\mathrm{ArN_2^+}$; aliphatic $\rightarrow \mathrm{N_2}+$ alcohol.
- **Sandmeyer vs. Gatterman:** CuX vs. Cu; both: $\mathrm{ArN_2^+} \longrightarrow \mathrm{Ar{-}X}$. Iodide via plain KI; fluoride via Balz–Schiemann ($\mathrm{HBF_4}/\Delta$).
- **Tests:** Hinsberg ($\mathrm{PhSO_2Cl}$) distinguishes $1^\circ/2^\circ/3^\circ$; carbylamine ($\mathrm{CHCl_3/KOH}$) confirms 1°; azo coupling of $\mathrm{ArN_2^+}$ with phenol/aniline gives dyes.

End of NCERT Exemplar Problems (Complete Set, 77 Questions)