#453400

Topic: Amines - Classification, nomenclature and isomerism

Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.

(i) $(CH_3)_2CHNH_2$ (ii) $CH_3(CH_2)_2NH_2$

(iii) $CH_3NHCH(CH_3)_2$ (iv) $(CH_3)_3CNH_2$

(v) $C_6H_5NHCH_3$ (vi) $(CH_3CH_2)_2NCH_3$

(vii) $m-BrC_6H_4NH_2$

Solution

The IUPAC names along with the classification are given below:

(i) 1-Methylethanamine (primary amine)

(ii) Propan-1-amine (primary amine)

(iii) N-Methyl-2-methylethanamine (secondary amine)

(iv) 2-Methylpropan-2-amine (primary amine)

(v) N-methylbenzenamine or N-methylaniline (secondary amine)

(vi) N-Ethyl-N-methylethanamine (tertiary amine)

(vii) 3-Bromobenzenamine or 3-bromoaniline (primary amine)

#453412

Topic: Chemical reactions of amines

Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine (ii) Secondary and tertiary amines

(iii) Ethylamine and aniline (iv) Aniline and benzylamine

(v) Aniline and N-methylaniline.

Solution

(i) Methylamine and dimethylamine :

Carbylamine test.

Methyl amine, on heating with alc. KOH solution and chloroform forms foul smelling methyl isocyanide. This test is not given by dimethylamine.

(ii) Secondary and tertiary amines :

Secondaty amines give libermann nitrosoamine test.

On heating with nitrous acid (prepared in situ), they give yellow coloured oily N-nitrosoamine.

Tertiary amines do not give such test.

(iii) Ethylamine and aniline :

Azo dye test.

Aniline on diazotization (ice cold nitrous acid solution) followed by coupling with 2-naphtol (in alkaline solution) forms brilliant orange or red dye. Ethylamine will not form dye. I will give brisk effervescence (due to liberation of nitrogen gas) but solution remains clear.

(iv) Aniline and benzylamine :

Azo dye test.

Aniline on diazotization (ice cold nitrous acid solution) followed by coupling with 2-naphtol (in alkaline solution) forms brilliant orange or red dye. Benzylamine will not give suc test.

(v) Aniline and N-methylaniline :

Carbylamine test.

Aniline, on heating with alc. KOH solution and chloroform forms foul smelling methyl isocyanide. This test is not given by N-methylaniline.

#453418

Topic: Chemical reactions of amines

Account for the following:

(i) pK_b of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

(iv) Although amino group is $o-$ and $p-$ directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

Solution

(i) pK_b of aniline is more than that of methylamine.

In aniline, the lone pair of electrons on N atom is in resonance with benzene ring. Hence, it cannot be easily donated to an acid. This decreases its basicity. In methyl amine, th $+I$ effect of methyl group increases the electron density on N atom so that the lone pair of electrons on N atom can be easily donated to an acid. Hence, methylamine is mor basic than aniline. Higher is the basicity, lower is the pKa and vice versa.

(ii) Ethylamine is soluble in water whereas aniline is not. With increase in the molecular weight, the solubility decreases. Aniline has higher molecular weight than ethylamine.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide. Due to the $+I$ effect of $-CH_3$ group, methylamine is more basic than water. Therefore in water, methylamine produces OH^- ions by accepting H^+ ions from water. OH^- ions react with ferric chloride to precipitate hydrated ferric oxide.

(iv) Although amino group is o and p directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of $m-$ nitroaniline. In acidic mediu the N atom of aniline is protonated to form anilinium ion. $Ph-NH_2+H^+ \rightarrow Ph-NH_3^+$Electron withdrawing $-NH_3^+$ group is meta directing.

(v) Aniline does not undergo Friedel-Crafts reaction. The lone pair of nitrogen present in aniline reacts with $AlCl_3$ to form an insoluble complex.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines. Diazonium salts of aromatic amines shows resonance stabilization. No such resonance stabilization is present in aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesizing primary amines. Over alkylation is avoided. Secondary and tertiary amines are not obtained.

#453427

Topic: Chemical reactions of amines

Arrange the following

(i) In decreasing order of the pK_b values: $C_2H_5NH_2, C_6H_5NHCH_3, (C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength: $C_6H_5NH_2, C_6H_5N(CH_3)_2, (C_2H_5)_2NH$ and CH_3NH_2

(iii) In increasing order of basic strength:

(a) Aniline, p-nitroaniline and p-toluidine

(b) $C_6H_5NH_2, C_6H_5NHCH_3, C_6H_5CH_2NH_2$

(iv) In decreasing order of basic strength in gas phase: $C_2H_5NH_2, (C_2H_5)_2NH, (C_2H_5)_3N$ and NH_3

(v) In increasing order of boiling point: $C_2H_5OH, (CH_3)_2NH, C_2H_5NH_2$

(vi) In increasing order of solubility in water: $C_6H_5NH_2, (C_2H_5)_2NH, C_2H_5NH_2$.

Solution

(i) Stronger base has lower pK_b value.

$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

(ii) Increasing order of basicity is as follows:

$C_6H_5NH_2 < C_6H_5NHCH_3 < CH_3NH_2 < (C_2H_5)_2NH$

(iii) Increasing order of basic strength.

(a) p-nitroaniline < aniline < p-toluidine

(b) $PhNH_2 < PhNHCH_3 < PhCH_2NH_2$

(iv) In decreasing order of basic strength in gas phase:

$Et_3N > Et_2NH > EtNH_2 > NH_3$

The stabilization of conjugate acids due to hydrogen bonding is absent.

(v) Increasing order of boiling point

$Me_2NH < EtNH_2 < EtOH$

(vi) Increasing order of solubility in water:

$PhNH_2 < Et_2NH < EtNH_2$

#453446

Topic: Chemical reactions of amines

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

Solution

Hinsberg's test is used for the identification of primary, secondary and tertiary amines.

Hinsberg's reagent is benzenesulphonyl chloride $(C_6H_5SO_2Cl)$.

It reacts differently with primary, secondary and tertiary amines.

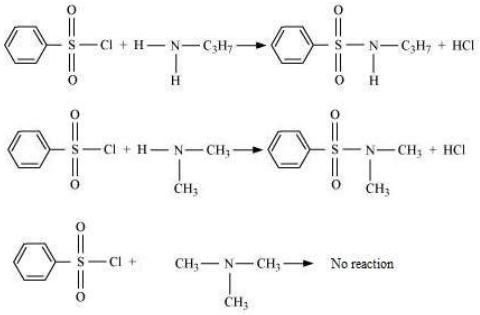
(i) Hinsberg's reagent reacts with primary amines to form $N-$ alkylbenzenesulphonyl amide which is acidic in nature and soluble in alkali.

Note: $N-$ alkylbenzenesulphonyl amide contains strong electron withdrawing sulphonyl group. Due to this, the $H-$ atom attached to nitrogen can be removed easily. Hence, is acidic.

(ii) Hinsberg's reagent reacts with secondary amines to form a sulphonamide which is insoluble in alkali.

Note: As there is no hydrogen atom attached to the N atom in the sulphonamide, it is not acidic and insoluble in alkali.

(iii) Hinsberg's reagent does not reacts with tertiary amines.



#453447

Topic: Diazonium salts

Write short notes on the following:

(i) Carbylamine reaction (ii) Diazotisation (iii) Hofmanns bromamide reaction

(iv) Coupling reaction (v) Ammonolysis (vi) Acetylation

(vii) Gabriel phthalimide synthesis.

Solution

(i) Carbylamine reaction

When aliphatic/ aromatic primary amines are heated with chloroform and alc KOH, foul smelling alkyl isocyanides or carbylamines are obtained. Secondary or tertiary amines d not give this test.

$$Ph-NH_2+CHCl_3+3KOH \xrightarrow{\Delta} Ph-NC+3KCl+3H_2O$$

(ii) Diazotisation

Aromatic primary amines react with nitrous acid in cold condition to form diazonium salts.

$$Ph-NH_2+NaNO_2+2HCl \rightarrow 273-278\,K Ph-N_2^+Cl^-+NaCl+2H_2O$$

(iii) Hofmanns bromamide reaction

Treatment of an amide with bromine and aqueous or alcoholic NaOH solution gives primary amine containing one carbon atom less.

$$Ph-CONH_2+Nr_2+4NaOH \rightarrow Ph-NH_2+Na_2CO_3+2NaBR+2H_2O$$

(iv) Coupling reaction

Arenediazonium salt reacts with aromatic compounds to give azo compounds having the general formula $Ar-N=N-Ar'$. The azo compounds are brightly coloured and used as dyes.

$$ArN_2^++Ar'H \rightarrow Ar-N=N-Ar'+H^+$$

(v) Ammonolysis

Any reaction with ammonia, analogous to hydrolysis, in which a bond is broken and an amino group is added to one fragment.

$$R-Cl+NH_3 \rightarrow R-NH_2\cdot HCl$$

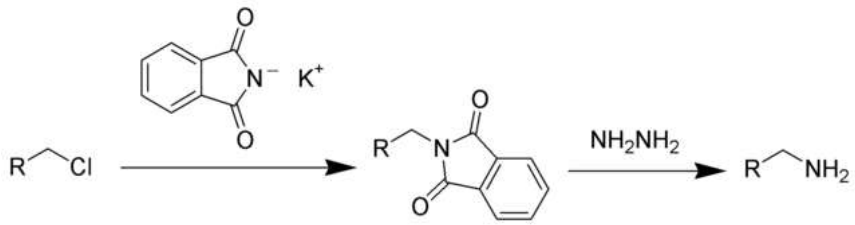
(vi) Acetylation

Alcohol reacts with acetyl chloride in presence of pyridine to form an ester. An acetyl group is introduced.

$$CH_3-CH_2-OH+CH_3-COCl \xrightarrow{pyridine} CH_3-CO-O-CH_2-CH_3+HCl$$

(vii) Gabriel phthalimide synthesis.

Phthalimide reacts withethanolic KOH followed by reaction with alkyl halide to form N-alkyl phthalimide. Hydrolysis with hydrazine gives primary amine. The reaction is shown i the image.



#453472

Topic: Methods of preparation of amines

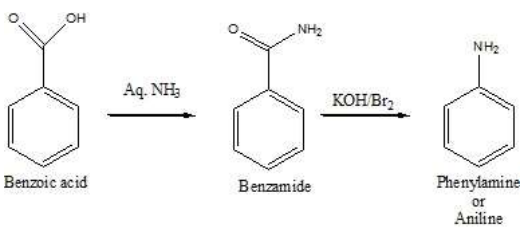
An aromatic compound A on treatment with aqueous ammonia and heating forms compound B which on heating with Br_2 and KOH forms a compound C of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

Solution

The aromatic compound A is benzoic acid C_6H_5COOH.

On treatment with aqueous ammonia and heating forms compound B, which is benzamide $C_6H_5CONH_2$.

Benzamide on heating with bromine and KOH forms a compound C of molecular formula C_6H_7N, which is aniline $C_6H_5NH_2$. The reaction is called Hoffmann bromamide degradation.



#453473

Topic: Diazonium salts

Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + alc.\ KOH \longrightarrow$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

(iii) $C_6H_5NH_2 + H_2SO_4(conc.) \rightarrow$

(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$

(v) $C_6H_5NH_2 + Br_2(aq) \rightarrow$

(vi) $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$

(vii) $C_6H_5N_2Cl \xrightarrow[(ii)\ NaNO_2/Cu,\ \triangle]{(i)HBF_4}$

Solution

Completed reactions are as shown.

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

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow C_6H_6(benzene) + N_2 + H_3PO_3 + HCl$

(iii) $C_6H_5NH_2 + H_2SO_4(conc.) \rightarrow C_6H_5NH_3^+HSO_4^-(anilinium\ hydrogensulphate)$

(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow C_6H_6(benzene) + CH_3CHO(ethanal) + N_2 + HCl$

(v) $C_6H_5NH_2 + Br_2(aq) \rightarrow 2,4,6 - Br_3 - C_6H_2 - NH_2(2,4,6 - tribromoaniline)$

(vi) $C_6H_5NH_2 + (CH_3CO)_2O \xrightarrow{CH_3COOH} C_6H_5CONHCH_3(Acetanilide) + CH_3COOH$

(vii) $C_6H_5N_2Cl \xrightarrow[(ii)\ NaNO_2/Cu,\ \triangle]{(i)HBF_4} C_6H_5NO_2(nitrobenzene) + BF_3 + NaF$

#453481

Topic: Methods of preparation of amines

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

Solution

During Gabriel phthalimide synthesis, the reaction between phthalimide and ethanolic potassium hydroxide gives potassium salt of phthalimide.

The salt on heating with alkyl halide followed by alkaline hydrolysis gives corresponding primary amine.

Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis as aryl halides do not undergo nucleophilic substitution with the salt formed by phthalimide.

#453482

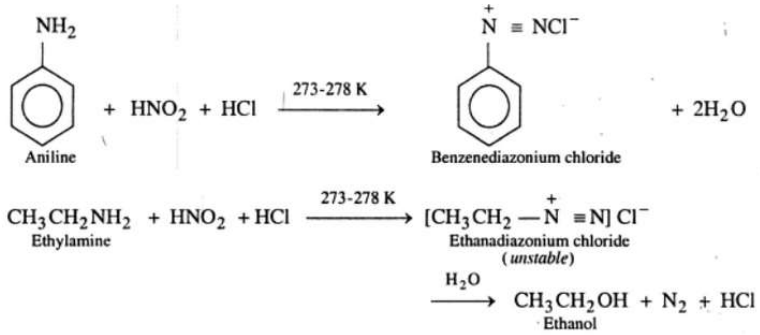
Topic: Diazonium salts

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

Solution

The reaction of aromatic primary amines with nitrous acid gives aromatic diazonium salts.

The reaction of aliphatic primary amines with nitrous acid gives aromatic diazonium salts which decompose to form a mixture of compounds containing alkyl chlorides, alkenes and alcohols. Usually, alcohols are the major products. The reactions are shown above.



#453484

Topic: Physical properties of amines

Give plausible explanation for each of the following:

(i) Why are amines less acidic than alcohols of comparable molecular masses?

(ii) Why do primary amines have higher boiling point than tertiary amines?

(iii) Why are aliphatic amines stronger bases than aromatic amines?

Solution

(i) Amines lose a proton to form amide ion. Alcohols lose a proton to form alkoxide ion.

$RNH_2 \rightarrow RNH^- + H^+$
$R-OH \rightarrow R-O^- + H^+$
O is more electronegative than N, the negative charge is more easily accomodated in RO^- than in $R-NH^-$. Hence, amines are less acidic than alcohols of comparable molecular masses.

(ii) In primary amines, N atoms have two H atoms which results in extensive intermolecular H bonding. In tertiary amines, N atoms do not have H atoms and hydrogen bondir is not possible.

Hence, primary amines have higher boiling point than tertiary amines.

(iii) Aliphatic amines stronger bases than aromatic amines due to following reasons:

(a) Aromatic amines have resonance due to which lone pair of electrons on N atom is delocalized over benzene ring and is less available for protonation.

(b) The stability of aryl amine ions is lower than the stability of alkyl amines. Protonation of aromatic amines is not favoured.