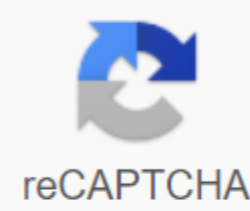




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Ans: Eight isomeric amines are possible isomerism exposed to various isomers of amines Chain: i) and ii) ; (iii) and (iv) ; (i) and (iv) Positional isomers: (ii) and (iii) ; (ii) and (iv) Metamers: (v) and (vi) ; (vii) and (viii) Functional isomers: All three types of amines are functional isomers with each other. 13.3. How do you convert: (i) Benzene to aniline (ii) Benzene to N,N-dimethylaniline (iii) Cl-(CH2)4-Cl to Hexane -1,6-diamine Ans: 13.4. In increasing order of their basic strength: (i) C2H5NH2, C6H5NH2, NH3, C6H5CH2NH2, (C2H5)2NH ii) C2H5NH2, (C2H5)2NH, (C2H5)3N, C6H5NH2 iii) CH3NH2, (CH3)2NH, (CH3)3N, C6H5NH2, C6H5CH2NH2 Ans: In general, the basic nature of ammonia (NH3) and amines is associated with the availability of a pair of lone electrons on a nitrogen atom. In other words, these are all Lewis bases. Amines act as Lewis bases due to the presence of a lone electron pair on a nitrogen atom. Since the nitrogen atom is sp<sup>3</sup> hybridized, its electron attracting tendency is significantly reduced. It can easily lose its electron pair and acts as a base. For example, amines form hydroxides with water. Here K<sub>t</sub> is called the dissociation constant for the base. A larger K<sub>b</sub> stronger value will be the basis. The basic strength of amines can also be expressed as pK<sub>b</sub> related to K<sub>b</sub> as : K<sub>b</sub> values are : 13.5. Complete the following acid-based reactions and replace the products: (i) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>+HCl ———> (ii) (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N+HCl ———> Ans: 13.6. Record the reactions of the final alkyl aniline product with excess methyl cyanide in the presence of sodium carbonate solution. ANS: 13.7. Write down the chemical reaction of aniline benzoyl chloride and type the name of the product obtained. ANS: 13.8. Write the structures of the different isomers corresponding to the molecular formula C<sub>3</sub>H<sub>9</sub>N. Write IUPAC names of isomers that liberate N<sub>2</sub> gas for nitric acid treatment. Ans: In all, four structural isomers are possible. They are: 13.9. Convert: (i) 3-methylaniline into 3-nitrotoluene (ii) Aniline to 1,3,5-Tribromo benzene Ans: NCERT EXERCISES 13.1. Write the IUPAC names of the following compounds and include them in primary, secondary and tertiary amines. (i) (CH<sub>3</sub>)<sub>2</sub>CHNH<sub>2</sub> (ii) CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub> (iii) CH<sub>3</sub>NHCH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub> (iv) (CH<sub>3</sub>)<sub>3</sub>CNH<sub>2</sub> (v)

C6H5NHCH3(vi) (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>3</sub> vii) m-BrC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> Ans: (i) Propan-2-amine[1°] (ii) Propan-1-amine (1°), (iii) N-Methylpropan-2-amine (2°), (iv) 2-methylpropan-2-amine(1°) (v) N-Methylbenzenamine or N-methylaniline (2°) vi) N-Ethyl-N-methylethanamine (vii) 3-bromobenzenamine or 3-bromaniline (1°) 13.2. Indicate 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. ANS: 13.3. Consider the following (i) pK<sub>b</sub> aniline is more than methylamine (ii) Ethylamine is water soluble, while aniline is not. (iii) Methylamine in water reacts with iron chloride to precipitate iron oxide. (iv) Although the amino acid o and p - directed in aromatic electrophilic substitution reactions, aniline on nitric acid gives a significant amount of m-nitroaniline. In Aniline will not undergo Friedel-Crafts reaction. (v) Diazonium salts of aromatic amines are more stable than aliphatic amine salts. (vi) Gabriel's synthesis of phthalimide is preferred for the synthesis of primary amines. ANS: (i) In aniline, a lone pair of electrons on the N-atom moves to the benzene ring. As a result, the density of electrons on nitrogen atom decreases. While in the CH<sub>3</sub>NH<sub>2</sub> group, +I-effect -CH<sub>3</sub> increases the density of electrons on the N-atom. Therefore, aniline is a weaker base than methylamine and therefore its pK<sub>b</sub> value is higher than that of methylamine. (ii) Ethylamine is dissolved in water due to the intermolecular bonding of H. (iii) Methylamine is more than water, receives proton from water liberating OH<sup>-</sup> ions, (iv) Nitration is usually carried out by a mixture of HNO<sub>3</sub> + conc. H<sub>2</sub>SO<sub>4</sub>. In the presence of these acids, most aniline is protonated. Therefore, in the presence of acids, the reaction mixture consists of aniline and anilinium ions. Now, the -NH<sub>2</sub> group in aniline is activating and ortho, p-directed, while the -NH<sub>3</sub> group in anilinium ion is deactivating and para-directed: Nitration of aniline (due to steric obstacles in ortho-positions) mainly gives p-nitroaniline, nitration of anilinium ion gives m-nitroaniline. In fact, approximately a mixture of p-nitroaniline and m-nitroaniline 1:1 is obtained. Thus, the nitration of aniline gives a significant amount of m-nitroaniline due to the protonation of the amino acid. 13.4. Arrange the following: (i) In descending order of pK<sub>b</sub> values: C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH and C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> (ii) In increasing order of basic strength: C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>2</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH and CH<sub>3</sub>NH<sub>2</sub>. (iii) In increasing order of the basic strength: (a) Aniline, p-nitroaniline and p-toluidine (b) C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub> (iv) In descending order of the basic strength in the gas phase: C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH, (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N and NH<sub>3</sub> (v) In increasing order of boiling point: C<sub>2</sub>H<sub>5</sub>OH, (CH<sub>3</sub>)<sub>2</sub>NH, C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> (vi) In increasing order of solubility in water: C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH, C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> ANS: (i) Due to the delocalisation of a lone pair of N-atom electrons above the benzene ring C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub> are much less basic than C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH. Due to the +I-effect -CH<sub>3</sub> group, the C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub> is slightly more basic than C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>. Between C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH is more basic than C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> due to the greater +I-effect of the two groups -C<sub>2</sub>H<sub>5</sub>. Therefore, the correct order of decreasing pK<sub>b</sub> values is: (i) Between CH<sub>3</sub>NH<sub>2</sub> and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH, mainly due to the greater +I-effect of the two groups -C<sub>2</sub>H<sub>5</sub> in one group -CH<sub>3</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH is more fundamental than CH<sub>3</sub>NH<sub>2</sub>. In both C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>2</sub> the lone pair of electrons present on the N-atom is redistributed through the benzene ring, but C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>2</sub> is more basic due to the +I effect of the two -CH<sub>3</sub> groups. (ii) (a) The presence of the electron donation group -CH<sub>3</sub> increases, while the presence of the electron withdrawal group -NO<sub>2</sub> reduces the basic strength of the amines. (b) In C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub>, N is directly connected to the benzene ring. As a result, a lone pair of electrons on the N-atom is penetrated through the benzene ring. Both C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub> are therefore weaker bases compared to C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub>. Between C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub>, due to the +I effect -CH<sub>3</sub> group C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub> is more basic. (iv) In the gas phase or in non-aqueous solvents such as chlorobenzene, etc., there is a lack of effects on the saute, i.e. stabilisation of conjugate acid due to H-bonding. +I-effect increases with an increase in the number of alkyl groups. Thus, the correct order of reduction of the basic force in the gas phase is, (v) Since electronegativity O is higher than that of N, alcohols form stronger H-bonds than amines. The range of H-bonding also depends on the number of H atoms on the N-atom, so the H-sticking range is greater in the primary amine than Amine. (vi) Solubility decreases with an increase in the molecular weight of the amines due to an increase in the size of the hydrophobic hydrocarbon part and with a decrease in the number of H-atoms on the N-atom that pass through the H-bonding. 13.5. How do you convert: (i) ethane acid to methanamine (ii) hexanenitrile to 1-aminopentane (iii) methanol to ethane acid. (iv) Etanamine to methanamine (v) Ethanic acid to propanic acid (vi) Methanamine to ethane (vii) nitromethane to dimethylamine (viii) propanic acid to ethanic acid? ANS: 13.6. Describe the method of identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved. A: Resolution in three types of amines can be made by the following methods: (i) the Hinsberg test: This is a very useful test for distinguishing primary, secondary and tertiary amines. Shake the amine with Hinsberg reagent (benzene sulfonyl chloride) in the presence of an excess of KOH aqueous solution. The reactions that will take place are listed on the next page. The primary amine is N-alkyl benzene sulphonamide, which dissolves in KOH aqueous solution to form potassium salt and regenerates insoluble sulphonamide after acidification with dilute HCl. The secondary amine consists of N, N - dialkyl benzene sulphonamide, which remains unreactive in aqueous KOH and even after acidification with dilute HCl tertiary amine does not react with benzene sulfonyl chloride and remains unreactive in aqueous KOH. However, for acidification diluted HCl gives a clear solution due to the formation of ammonium salt. (ii) Nitric acid reaction: All three types of amines, both aliphatic and aromatic, react with nitric acid under different conditions to produce different products. As nitrous acid is highly unstable, it is prepared in situ by the dosing of dilute hydrochloric acid for sodium nitrite. (a) Primary aliphatic amines react with low-temperature nitric acid (cold conditions) to produce primary alcohol and nitrogen gas accompanied by a brisk effervescence. Nitrous acid is unstable in nature and is prepared in situ by reaction of sodium nitrite with dilute hydrochloric acid. For example, the reaction is used as a test for primary aliphatic amines as no other amine develops nitrogen with nitrous acid. (b) Primary aromatic amines such as aniline react with nitric acid under cold conditions (273-278 K) to form benzene diazonium salts. The reaction is known as a diazotisation reaction. In the event that the temperature can climb above 278 K, benzene diazonium chloride is broken down with water and forms phenol. Aliphatic primary amines also react with nitrous acid to create alkyl diazonium salts in a similar way. But these are quite unstable and break down to form a mixture of alcohols, alkyne and alkyl halides along with the development of N<sub>2</sub> gas. (c) Secondary aliphatic and aromatic amines react with nitric acid to produce nitrosamines which are separated as fatty liquids. (d) Tertiary aliphatic amines dissolve in a cold solution of nitrous acid and form salts that break down into warming to make nitrosamine and alcohol. For example, tertiary aromatic amines react with nitric acid to give a dyed nitrosoderivative. This reaction is called nitrosation and as a result, the hydrogen atom in the steam position is replaced by a nitroso (-NO) group. For example, 13.7. Write short notes on the following: (i) Carbylamine reaction (ii) Diazotisation (iii) Hofmann bromamide reaction (iv) Clutch reaction (v) Ammonolysis (vi) Acetylation (vii) Synthesis of Gabriel phthalimide ANS: (i) Carbylamine reaction: Aliphatic and aromatic primary amines when heated with chloroform and alcoholic KOH solution, produce isocyanides or carbylamines that have very unpleasant odors. This reaction is called carbylamine reaction. (ii) Diazotisation: The process of converting a primary aromatic amino acid into diazonium salt is known as diazotisation. This process is carried out by adding an aqueous solution of sodium nitrite to a solution of primary aromatic amine (e.g. aniline) exceeding HCl at a temperature below 5°C. (iii) Hoffmann bromamide reaction: When treated with bromine in an alkaline solution, it is returned to a primary amine with one carbon atom smaller than the amide. This reaction is known as Hoffmann's reaction to bromamide degradation. (iv) Coupling reactions: In this reaction, diazonium salt reacts with an aromatic amino acid (in acid medium) or phenol (in an alkaline medium) to form brightly coloured azo compounds. The reaction is generally carried out in the steam position on hydroxy or amino acids. If the steam position is blocked, it occurs in the ortho position and if both the ortho and steam positions are occupied before there is any connection. In Ammonolysis: This is the process of replacing either halogen alkyl halide atom (or arylhalide) or hydroxyl group in alcohols (or phenols) with an amino group. The agent used for ammonolysis is alcoholic ammonia. In general, a mixture of primary, secondary and tertiary amine is formed. (vi) Acetylation: The process of introducing the acetyl (CH<sub>3</sub>CO-) group into the molecule using acetyl chloride or acetic anhydride is called acetylation. (vii) Synthesis of Gabriel phthalimide: It is a method of preparation of pure aliphatic and aralkyl primary amines. Phthalimide in the treatment of ethanolic KOH gives phthalimide potassium, which when heated with appropriate alkyl or aralkyl halides gives N-substituted phthalimides, which give primary amines when hydrolysed with an HCl dilator or alkaline. 13.8. Carry out the following conversions: (i) nitrobenzene to benzoic acid (ii) Benzene to m-bromophenol (iii) benzoic acid to aniline (iv) Aniline to 2,4,6-trichloroaniline (iii) aniline (iv) Aniline to 2,4,6-trichloroaniline (2,4,6-trichloroaniline) (v) Benzyl chloride to 2-phenylethanamine (vi) chlorobenzene to p-chloroaniline (vii) Aniline to p-bromoaniline (viii) Benzamide to toluene (ix) Aniline to benzyl alcohol. 13.9. Indicate structures A, B and C in the following response: ANS: 13.10. Aromatic compound A, when treated with aqueous ammonia and heating, forms compound B, which, when heated, Br<sub>2</sub> and KOH form compound C of molecular formula C<sub>6</sub>H<sub>7</sub>N. Write the structures and names of IUPAC compounds A, B and C. ANS: From the information available, we find that B when heated with Br<sub>2</sub> and KOH forms compound C. Since B was formed when compound A was heated with aqueous ammonia, compound A is an aromatic acid. It's benzoic acid. The above reactions are given as follows: 13.11. Fill in the following reactions: ANS: 13.12. Why can't I prepare aromatic primary amines by synthesising Gabriel phthalimide? ANS: The success of Gabriel phthalimide's response depends on a nucleophilic attack of phthalimide anion on an organic halogen compound. Since aryl halides have not passed nucleophilic substitution reactions easily, arylamines, i.e. aromatic, primary amines cannot be prepared by Gabriel phthalimide reaction. 13.13. Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitric acid. ANS: Both aromatic and aliphatic primary amines react with HNO<sub>2</sub> at 273-278 K to create aromatic and aliphatic diazonium salts. But aliphatic diazonium salts are unstable even at this low temperature, so they easily break down to form a mixture of compounds. Aromatic and aliphatic primary amines react with 13.14. Please provide a plausible explanation for each of the following options: (i) Why are amines less acidic than alcohols of comparable molecular weights? (ii) Why do primary amines have a higher boiling point than tertiary amines? (iii) Why are aliphatic amines stronger than aromatic amines? ANS: (i) Loss of amine proton gives amid ion, while loss of proton from alcohol gives alkoxide ion. R-NH<sub>2</sub> —> R-NH<sup>-</sup> +H<sup>+</sup> R-O —> R-O<sup>-</sup> +H<sup>+</sup>. Since O is more electronegative than N, so does it will attract positive species more strongly compared to N. So, RO<sup>-</sup> is more stable than RNH<sup>-</sup>. This means that alcohols are more acidic than amines. On the contrary, amines are less acidic than alcohols. (ii) Due to the presence of two H-atoms on the N-atom of primary amines, they undergo extensive intermolecular H-bonding, while tertiary amines do not undergo H-bonding due to the absence of an H-atom in the N-atom. As a result, primary amines have higher boiling points than tertiary amines of comparable molecular weight. (iii) Aromatic amines are much less basic than ammonia and aliphatic amines for the following reasons: (a) Due to resonance in aniline and other aromatic amines, a lone pair of electrons on a nitrogen atom is delocalised into the benzene ring and is therefore less readily available for protonation. Aromatic amines are therefore weaker than ammonia and aliphatic amines. (b) Aromatic amines (arS) are more stable than corresponding protonated ions; therefore, they have a very less tendency to combine with proton to form protonated ions, and so are less basic. More resources for CBSE Class 12: NCERT Solutions Maths Physics Chemistry Biology Science

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