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Electrophilic Aromatic Substitution Reactions are those organic reactions in which an electrophile replaces one or more hydrogen atoms linked to an aromatic ring. These reactions include the substitution of a hydrogen atom from a benzene ring with an electrophile. Aromatic nitrations, aromatic sulphonation, and Friedel-Crafts reactions are examples. The aromaticity of the aromatic system is conserved in an electrophilic aromatic substitution process. When bromobenzene is made from the reaction of benzene and bromine, for example, the aromatic ring remains stable. Aryl halides or haloarenes can be produced through electrophilic aromatic halogenation reactions of aromatic rings with iodine, chlorine, or bromine. Key Terms: Electrophilic Substitution, Substitution Reaction, Chiral Carbon, Aromatic Ring, Phenols, Benzene, Electron, Nitration, Halogenation [Click Here for Sample Questions] Because of their high electron density, phenols are prone to electrophilic substitution reactions. In phenol, the hydroxyl group linked to the aromatic ring promotes efficient charge delocalization in the aromatic ring. As a result, it uses resonance to stabilize the arenium ion. The hydroxyl group also produces ortho para directors. Read More: Nitration of Phenols [Click Here for Sample Questions] After being treated with weak nitric acid, phenols are nitrated at a low temperature (298 K), yielding a mixture of ortho and para nitrophenols. Based on their volatility, the resulting mixture is further separated into ortho and para nitrophenols by steam distillation. Ortho nitrophenols, which include both intramolecular and intermolecular hydrogen bonding, are less volatile than para nitrophenols, which solely involve intermolecular hydrogen bonding. Nitration of Phenols When phenol is treated with strong nitric acid, 2, 4, 6-trinitrophenol is formed as a result of the nitration (commonly called picric acid). Formation of 2, 4, 6-trinitrophenol Halogenation of Phenols [Click Here for Sample Questions] Even in the absence of Lewis acids, phenols undergo halogenation due to the highly activating impact of the hydroxyl group. Monobromophenols are generated when phenols are treated with bromine in the presence of a low-polarity solvent such as $CHCl_3$ at low temperatures. A white precipitate of 2, 4, and 6-tribromophenol is generated when phenol is treated with bromine water. Formation of 2, 4, 6-tribromophenol Kolbe’s Reaction [Click Here for Sample Questions] The phenoxide ion is generated when phenol is treated with sodium hydroxide. The generated phenoxide ion is extremely reactive in electrophilic substitution processes. It conducts an electrophilic substitution reaction with a weak electrophile (carbon dioxide) to create Ortho-hydroxybenzoic acid. Kolbe's reaction is the commonly used term or name for this reaction. Kolbe’s Reaction Reimer-Tiemann Reaction [Click Here for Sample Questions] An aldehyde group is generated at the ortho position of the benzene ring when phenol is treated with chloroform in the presence of sodium hydroxide. The Reimer-Tiemann reaction is a well-known name for this reaction. Reimer-Tiemann Reaction Question. When phenol is treated with excess of bromine water, it gives (a) m-bromophenol, (b) o- and p-bromophenols, (c) 2,4-dlbromophenol, (d)2,4,6-tribromophenol – [NEET 1992] Question. When phenol is treated with $CHCl_3CHCl_3$ and NaOH, the product formed is :- (a) Benzaldehyde, (b) Salicylaldehyde, (c) Salicylic acid, (d) Benzoic acid – [NEET 1980] Question. Reaction of phenol with chloroform in presence of dilute sodium hydroxide finally introduces which one of the following functional group? – [NEET 2015] Question. A is a lighter phenol and B is an aromatic carboxylic acid. Separation of a mixture of A and B can be carried out easily by using a solution of: (a) sodium hydroxide, (b) sodium sulphate, (c) calcium chloride, (d) sodium bicarbonate. – [NEET 1992] Things to Remember The organic reactions in which an electrophile replaces one or more hydrogen atoms linked to an aromatic ring are known as electrophilic aromatic substitution reactions. Phenols are effectively and highly prone to electrophilic substitution reactions due to their rich electron density. In phenols, the hydroxyl group attached to the aromatic ring, facilitates the effective delocalization of the charge in the aromatic ring. Therefore, it helps in stabilising the arenium ion through resonance. The hydroxyl group acts as ortho para directors, thus, most of these substitutions are at ortho and para positions only. Some of the electrophilic substitution reactions of phenols are Nitration of Phenols, Halogenation of Phenols, Kolbe’s Reaction, and Reimer-Tiemann Reaction. Also Read: Ques. Why phenol does not undergo electrophilic substitution? (3 Marks) Ans. The oxygen attaches to the C on the benzene ring due to the Resonance (+R) effect, forming a partial double bond that is difficult to break. It is tough to break the cycle. The bond length increases shorter when oxygen is linked to an sp3 hybridized carbon, making it more difficult to break. Due to repulsion, the approach of an electron-rich nucleophile to an electron-rich benzene ring is less likely. Ques. Why does phenol undergo an electrophilic substitution reaction at the ortho and para positions? (3 Marks) Ans. Because the lone pair on the oxygen atom stabilizes the intermediate carbocation, phenols undergo electrophilic substitution at ortho and para positions, the stability is greatest. As a result of the presence of the hydroxyl group, the ring is activated and reactive in both ortho and para positions. Ques. What is the electrophilic substitution reaction mechanism? (3 Marks) Ans. Electrophilic substitution reactions are chemical reactions in which an electrophile displaces a functional group in a molecule. Aromatic substitution reactions are frequent means of adding functional groups into benzene rings and are typical of aromatic compounds. Ques. Why Phenols are very reactive towards electrophilic aromatic substitution? (3 Marks) Ans. Because the nonbonding electrons on oxygen stabilize the intermediate cation, phenols are extremely reactive for electrophilic aromatic substitution. The hydroxyl group of phenol is believed to be activating (i.e., its presence causes the aromatic ring to be more reactive than benzene) and ortho- or para-directing since this stabilization is more effective for the attack at the ortho or para position of the ring. Ques. Why is Phenol more reactive than Benzene in electrophilic substitution reactions? (2 Marks) Ans. The -OH group on phenol and the lone pair of electrons on oxygen are given into the Benzene ring and activate it, making it more vulnerable to electrophile assault. Ques. What is the directing effect of phenol towards electrophiles? (3 Marks) Ans. Phenol is an ortho/para director, however, the reaction is faster in the presence of a base. This is owing to the phenolate anion's greater reactivity. The negative oxygen was 'pressed' to supply electron density to the carbons (it has an additional +I effect due to its negative charge). Ques. What is the bromination of phenol? (3 Marks) Ans. Bromination is a substitution process for phenol. Bromine is used to substitute hydrogen in the benzene ring of phenol. When phenol is treated with Br_2 in a water solvent, it produces a polybromo derivative with all hydrogen atoms in ortho, meta, and para positions with respect to the OH. Ques. What happens when phenol reacts with H_2SO_4? (3 Marks) Ans. Phenol combines with sulfuric acid to form substituted phenols when it reacts with concentrated sulphuric acid. At normal temperature, a combination of phenol sulphuric acid and the resulting benzene ortho hydroxy sulfuric acid reaches equilibrium. Ques. What is the oxidation of phenol? (3 Marks) Ans: The oxidation process begins with the decomposition of phenol into aromatic compounds with two hydroxyl groups replaced in the benzene rings (hydroquinone, resorcinol, and catechol). The oxidation of these molecules produces the quinone chemicals p-benzoquinone and o-benzoquinone. For Latest Updates on Upcoming Board Exams, Click Here: Check-Out: Quick Notes Reactions of Phenol The hydroxyl group (OH) in phenol ‘activates’ the benzene ring, making it more reactive with electrophiles. Phenol is able to react directly with bromine (unlike benzene) in multiple substitution reactions to produce 2,4,6-tribromophenol. Nitration of phenol is easier than the nitration of benzene. Only nitric acid (HNO_3) at room temperature is required (for nitration of benzene: nitric acid, sulfuric acid and temperature of 55oC). The OH group in phenol has a directing effect, meaning substitutions are most likely to occur on the second, fourth and sixth carbon (carbon one is occupied by the OH group). Full Notes Reactions of Phenol Phenol can react directly with bromine, whereas benzene is unable to. The hydroxide group is described as ‘activating’ because of the extra electron density it gives the delocalised electron ring, making the molecule more reactive with electrophiles. Bromination The increased electron density in the ring within phenol (see Phenol) enables the ring to polarise a bromine molecule enough to form an electrophile. Benzene does not have enough electron density in the ring for this to happen. This is why benzene needs a halogen carrier to react with bromine but phenol does not. A lone pair of electrons on the oxygen atom in phenol is donated or ‘merged’ into the pi-bonding system in the benzene ring. The electron density inside the benzene ring increases as a result; this increased electron density enables phenol to react with electrophiles more easily than benzene can. Phenol also undergoes multiple substitutions, forming 2,4,6-tribromophenol. Benzene only undergoes a single substitution, forming bromobenzene. Nitration of Phenol Just like with benzene, phenol can react with a nitronium ion ($NO^{+}2$), and a nitro group is added onto the carbon ring. As seen with bromination (see above), phenol is more reactive with electrophiles than benzene. So, the nitration of phenol happens more easily than the nitration of benzene. Room temperature and dilute nitric acid are the only reactants and conditions required (with the nitration of benzene, higher temperatures (55oC) and concentrated sulfuric acid are also necessary). Directing Effect of Phenol The positions that an electrophile substitutes to in phenol are as a result of electrons from the oxygen atom being moved around the ring. This detail is not needed for A-level Chemistry, but it does explain why the above occurs. If we draw out the Kekulé structure of the phenyl group (benzene ring) in phenol, it’s easier to see how the electrons from the negatively charged oxygen cause the positions of double bonds to move around the ring. The phenol dissociates in solution and releases a H^+ ion from the hydroxide group. The electrons added to the ring from the oxygen atom repel the electrons in the double bond nearest the carbon attached to the oxygen. The repulsion moves the electrons in the bond to the next carbon, making it negatively charged. This negatively charged carbon is more likely to bond with an electrophile than any other carbon atoms in the ring, this is why the electrophile bonds to the 2nd carbon. Making it 2-bromophenol in the case of bromination. The negative charge does not just remain on the 2nd carbon though – it causes repulsion with the next closest double bond, forcing those electrons onto the second furthest carbon (4th carbon), making the 4th carbon negatively charged. This 4th carbon is now the most likely to react with an electrophile, so the next electrophilic substitution takes place on the 4th carbon. This same process also occurs with the 6th carbon. The movement of charge around a molecule may look very strange (and for A-level students – you do not need to know this), but it is just a way to show how the charge can be spread around the molecule. The possible structures that result from the movement of delocalised electrons around a molecule are called resonance structures. Share — copy and redistribute the material in any medium or format for any purpose, even commercially. Adapt — remix, transform, and build upon the material for any purpose, even commercially. The licensor cannot revoke these freedoms as long as you follow the license terms. Attribution — You must give appropriate credit , provide a link to the license, and indicate if changes were made . You may do so in any reasonable manner, but not in any way that suggests the licensor endorses you or your use. ShareAlike — If you remix, transform, or build upon the material, you must distribute your contributions under the same license as the original. No additional restrictions — You may not apply legal terms or technological measures that legally restrict others from doing anything the license permits. You do not have to comply with the license for elements of the material in the public domain or where your use is permitted by an applicable exception or limitation . No warranties are given. The license may not give you all of the permissions necessary for your intended use. For example, other rights such as publicity, privacy, or moral rights may limit how you use the material. Sign Up Now &Daily Live Classes3000+ TestsStudy Material & PDFQuizzes With Detailed Analytics+ More BenefitsGet Free Access Now Phenols can be prepared industrially by a substitution reaction of aryl halides under extreme conditions: This is a type of nucleophilic aromatic substitution via benzyne intermediate: Milder conditions suitable for laboratory preparation of phenols are possible if there is an electron-withdrawing group on the ring that goes through the addition-elimination mechanism of nucleophilic aromatic substitution: Notice that increasing the number of electron-withdrawing groups decreases the required temperature. You can read more about the mechanism and radiochemistry of nucleophilic aromatic substitution here. In a similar nucleophile aromatic substitution, benzenesulfonic acid can be converted to phenol. The intermediates of this reaction are sodium benzenesulfonate sodium phenoxide: Another industrial method is the cumene (isopropylbenzene) process where phenol and acetone are prepared from benzene and propylene via a mechanism involving radical intermediates. Notice that the first step is a Friedel-Crafts alkylation. Anisole or other ether derivatives can be converted to phenol by acid-catalyzed cleavage: Phenols can also be prepared from benzene derivatives by converting them to an arene diazonium salt and subsequently hydrolyzing them: The addition of cuprous oxide can increase the yield of this reaction. Arene diazonium salts are excellent precursors in preparing various aromatic compounds and you can read about them in this dedicated article. Phenols in Electrophilic Aromatic Substitution Phenols are great substrates for halogenation, nitration, sulfonation, and Friedel–Crafts reactions as they often do not require a catalyst for electrophilic aromatic substitution. The OH group is an ortho, para director, and because of the strongly activating feature of the OH group: The ratio of the ortho and para substitution is difficult to predict. On one hand, the para position is favored because of the steric hindrance of the ortho position, on the other hand, there are two ortho positions and only one para, which statistically increases the yield of the ortho substitution. The larger the group present on the ring, the more favored the para substitution would be. The intermolecular interaction such as hydrogen bonding between the OH and the other group also contributes to the formation of the ortho isomer. Notice that Cl_2 and Br_2 react with phenol and other benzene derivatives with strongly activating groups such as NH_2 without a catalyst, and transubstantiation occurs. With nonactivated or deactivated aromatic compounds, the halogens require the presence of a Lewis acid catalyst ($AlCl_3$ or $FeBr_3$). Notice also that for the nitration of phenol, dilute nitric acid is used to avoid undesired oxidation reactions. A monobromination at the para position can be achieved by using one equivalent of Br_2 at lower temperatures (< 5 °C): Iodination of phenol and other benzene derivatives is more difficult because it is a very weak electrophile, and only reacts in the presence of silver(I) salts, HNO_3, or other oxidants. N-iodosuccinimide (NIS) and N-bromosuccinimide (NBS) have also been shown to work for the iodination and bromination of benzene derivatives. The reagent ICl is a better iodinating agent than molecular iodine. Fluorine, on the other hand, is too reactive and the reaction is vigorous with no practical use in laboratories. You can find more about the halogenation of arenes in March’s advanced organic chemistry. Why is OH a Strongly Activating Group? Due to the strong activating power, anisole undergoes nitration about 10,000 times faster than benzene and about 400 times faster than toluene. All the other electrophilic aromatic substituting reactions are also faster when oxygen or nitrogen is connected to the aromatic ring. Now, you may wonder why it is the case if they are more electronegative than carbon and should pull the electron density from the ring thus making it less reactive. Recall that the reason for such a strong activating power of the oxygen and nitrogen is the resonance stabilization of the cation by the nonbonding electrons which other activating groups such as alkyls do not have: So, even though oxygen pulls the electron density from the ring via the inductive effect, the +M mesomeric (electron-donating resonance) effect is more profound which makes it a strongly activating group. Friedel Crafts Reactions of Phenols Although phenols are Lewis bases, and the oxygen does bind to the Lewis acid catalyst, and the reactions may require higher temperatures, the Friedel-Crafts reactions are still possible, especially so for anisole where the methyl group protects the oxygen from the Lewis acid. This is not true for aniline, because nitrogen is a stronger base and binds to the Lewis acid catalyst making the ring completely unreactive. Oxidation of Phenols Phenols undergo oxidation in the presence of typical oxidizing agents such as chromic acid ($Na_2Cr_2O_7$ is the precursor) forming 1,4-conjugated diketones called quinones: Oxidation of hydroquinone (1,4-benzenediol) occurs even with milder oxidizing agents such as AgBr: The oxidation of phenols o quinones is reversible and plays an important role in the biochemical process as it serves as a transport for a pair of electrons from one substance to another in enzyme-catalyzed reactions. The Acidity of Phenols Because of the resonance stabilization of its conjugate-base anion, phenols are a lot more acidic than aliphatic alcohols: The presence of electron-withdrawing groups (EWG) increases the acidity even more a they help stabilize the negative charge of the phenoxide ions. As expected, having an electron-donating group on the ring reduces the acidity of phenol because it brings additional electron density rather than delocalizing it: Aside from the nature of the group, we need to also pay attention to its position – the orientation of the group relative to the OH group. For example, substituent groups can also affect phenol acidity by both polar and resonance effects. For example, p-nitrophenol is more acidic than m-nitrophenol even though the p-nitro group is farther from the phenol oxygen: This cannot be explained by the electronegativity of the nitro group since this effect gets smaller as the distance between the acidic proton decreases. And, as always, resonance stabilization comes to the rescue when explaining many features of organic molecules. When the nitro group is in the para position, it can participate in the delocalization of the lone pair on the nitrogen while, in the meta position, it cannot: A significant contribution of the highlighted resonance structure is that it places the negative charge on the more electronegative oxygen atoms which is not the case for the m-nitrophenol: Phenol as a Nucleophile The oxygen of the OH group in phenol is not as nucleophilic as it is in aliphatic alcohols because of the delocalization of the lone pairs and the steric effect of the aromatic ring, however, we can activate it by deprotonation to prepare a phenoxide ion which then reacts with electrophiles such as alkyl halides, acyl halides, acid anhydrides and etc.: Due to the high reactivity of acid chlorides, they can also react with phenol. Phenol as a Carbon Nucleophile The phenoxide ion also acts as a carbon nucleophile due to the resonance activation of the ring. For example, it is used as an industrial method for the preparation of salicylic acid (Kolbe-Schmidt reaction), which is then converted to aspirin (acetylsalicylic acid): Notice that, unlike monobromination, the carboxylation occurs at the ortho position which is due to the coordination of the carbon dioxide with the sodium: Check Also Phenol reacts with bromine water to give white ppt of 2,4,6-tribromophenol. Reason for tribromo substitution Phenol in the presence of water is converted into the phenoxide ion ($C_6H_5{-}O^-$) which is a strong activating species. Hence tribromo-substitution occurs. Monobromo phenol Bromine is added to a non-polar solvent like CS_2 or CCl_4 to form monobromo phenol. Nitration Phenol reacts with conc. HNO_3 to form 2,4,6-trinitrophenol. Dil. HNO_3 is used to get mononitro phenols. Reimer-Tiemann reaction Phenol reacts with chloroform ($CHCl_3$) in base (NaOH or KOH etc.) to form salicylaldehyde. If we use CCl_4 (carbon tetrachloride) instead of chloroform, salicylic acid is formed. Kolbe's reaction The reaction of phenoxide ion with CO_2 followed by acidification yields salicylic acid. This reaction is known as Kolbe's reaction. Coupling reaction Benzenediazonium salt reacts with phenol in weakly alkaline medium at low temperature (0-5° C) to form coloured products called azo dyes. This reaction is known as coupling reaction. Conversion Convert phenol to acetophenone Phenols can undergo many types of reactions as both the electron-rich benzene ring and the polar -OH group can participate in chemical reactionsSome of the reactions of phenols include:With basesWith reactive metalsWith diazonium saltsNitrationBrominationThe -OH group in phenols has a slightly acidic characterIt can therefore act as an acid and take part in acid-base reactionsPhenols are only slightly soluble in water due to the large non-polar benzene ringHowever, they do dissolve in alkaline solutions and undergo acid-base reactions with bases to form a soluble salt and waterPhenols are weak acids and undergo acid-base reactions in alkaline solutionsMolten phenols react vigorously with reactive metals such as sodium (Na)This is also an acid-base reactionNow, a soluble salt is formed and hydrogen gas is given offMolten phenols react vigorously with reactive metals to form a soluble salt and hydrogen gasReaction with diazonium ionsDiazonium ions are very reactive compounds containing an $-N_2^+$ groupWhen phenols are dissolved in sodium hydroxide (NaOH), a solution of sodium phenoxide is obtainedThis solution is cooled in ice and cold diazonium ion is added to the sodium phenoxideAfter the reaction has occurred, a yellow-orange solution or precipitate of an azo compound is formedThese are compounds in which two benzene rings are linked by a nitrogen bridgePhenol in diazonium ion reactionsAzo compounds are formed from the reaction of phenols with diazonium ionsReactions of the aromatic ring in phenolsPhenols react more readily with electrophiles compared to benzeneThis is because one of the lone pairs of electrons on the oxygen atom in -OH overlaps with the π bonding systemThis increases the electron density of the benzene ring making it more susceptible to electrophilic attackThe -OH group in phenols is activating and directs incoming electrophiles to the 2, 4, and 6 positionsNitrationPhenols can undergo electrophilic substitution reactions when reacted with dilute nitric acid (HNO_3) at room temperature to give a mixture of 2-nitrophenol and 4-nitrophenolWhen concentrated HNO_3 is used, the product will be 2,4,6-trinitrophenol insteadA hydrogen atom in the benzene ring is substituted by a nitro ($-NO_2$) groupThis is also known as the nitration of phenolPhenol in nitration reactionsPhenols undergo nitration when reacted with dilute HNO_3 at room temperatureBrominationPhenols also undergo electrophilic substitution reactions when reacted with bromine water at room temperaturePhenol decolourises the orange bromine solution to form a white precipitate of 2,4,6-tribromophenolThis is also known as the bromination of phenolPhenol in bromination reactionsPhenols undergo bromination when reacted with bromine water at room temperaturePage 2Although phenol compounds contain an alcohol (-OH) group, they are weakly acidicThis is due to the delocalisation of one of the lone pairs from the oxygen atom into the aromatic ringThis increases the electron density of the ring and increases the acidic behaviourThe conjugate base of phenol is the phenoxide ionIn the phenoxide ion, the negative charge on the oxygen is spread out over the entire ionThis is possible as one of the lone pairs on the oxygen atom overlaps with the delocalised π system of the ringBecause of this delocalisation, there is less charge density on the oxygen atomThe H^+ ions are therefore not strongly attracted to the phenoxide ion and are less likely to reform the phenol moleculeThis means that phenol is more likely to lose a proton (and act as an acid) rather than to gain a proton (and act as a base)The negative charge is spread over the ion, causing the electrons to become less available for bonding with an incoming protonStability of the conjugate basePhenol ionises to form a more stable negative phenoxide ion with its negative charge spread outThis means that phenol is more likely to undergo ionisationThe equilibrium position, therefore, lies further to the right and a higher proportion of phenol molecules donate a proton compared to for example water and ethanolThe phenol compound is, therefore, more likely to act as an acid rather than a baseTherefore, the position of equilibrium lies:Further to the right-hand side favouring the dissociated phenoxide ionsFurther to the left-hand side favouring the undissociated ethoxide and hydroxide ionsThe equilibrium position of phenol and the phenoxide ionSince the phenoxide ion formed from the ionisation of phenol is more stable than phenol itself, the equilibrium position lies further to the right-hand-side and phenol is more likely to act as an acid rather than a baseThe pKa is a measure of the acidity of a substanceThe values of water, phenol, and ethanol show that phenol is a stronger acid than ethanol and waterAcidDissociationpKa at 25 oCEthanolC_2H_5OH (aq) $C_2H_5O^-$ (aq) + H^+ (aq) 16WaterH_2O (l) OH^- (aq) + H^+ (aq)14Phenol C_6H_5OH (aq) $C_6H_5O^-$ (aq) + H^+ (aq)10The order of acidity can be explained by looking at their conjugate bases which are formed from the dissociation of the compoundsIn the phenoxide ion (which is the conjugate base of phenol) the charge density on the oxygen atom is spread out over the entire ionAs a result, the electrons on the oxygen atom are less available for bond formation with a proton (H^+ ion)The conjugate base of ethanol is the ethoxide ionThe ethyl group in the ion is an electron-donating group that donates electron density to the oxygen atomAs a result, the electron density on the oxygen atom is more readily available for bond formation with a H^+ ionThe electron-donating alkyl group in the ethoxide ion concentrates charge density on the oxygen atom which can more easily bond an H^+ ionThe conjugate base of water is the hydroxide ionSince the charge density of the oxygen atom cannot become delocalised over a ring, the hydroxide ion more readily accepts an H^+ ion compared to the phenoxide ionWater is, therefore, a stronger base compared to phenolHowever, as there are no electron-donating alkyl groups, less negative charge is concentrated on the oxygen atom which therefore less readily accepts an H^+ ion compared to the ethoxide ionWater is, therefore, a weaker base compared to ethanolThe equilibrium between water and the hydroxide ionThe hydroxide ion lacks an aromatic ring and electron-donating alkyl groups so water is a stronger base than phenol but a weaker base than ethanolTherefore, the position of equilibrium lies:Further to the right-hand side favouring the dissociated phenoxide ionsFurther to the left-hand side favouring the undissociated ethoxide and hydroxide ionsRelative equilibrium positions for the dissociation of ethanol, water and phenolThe relative equilibria for the dissociation of ethanol, water and phenol mean that ethanol is the weakest acid, while phenol is the strongest acid Did this page help you? Phenols are organic hydrocarbon compounds with a hydroxyl group directly attached to an aromatic hydrocarbon compound like Benzene Ring. Phenols are also termed as Phenolic compounds. The molecular the formula of phenols is $C_6H_5O_6$. The synthesis of Phenols is Natural as well as artificial. Electrophilic substitution reaction is one of the most important chemical properties of phenols. The phenols are compounds in which the hydroxyl atom is attached to the aromatic Benzene atom. The OH atom in the phenol is attached to the sp2 carbon atom of the benzene ring. The sp2 hybridized is highly electro negative in nature. As a result of this the electron density of the Oxygen atom of the phenols. This makes the phenoxide ion more attackable by an electrophile. The rearrangement of electrons in the phenol compound is one of the reasons for the proper electrophilic substitution reactions. In the rearrangement of electrons in the phenols, the electron cloud gets rearranged and shifted to the sp2 hybridized carbon atom of the benzene ring. This is because of the higher electronegativity of the sp2 hybridization assays of the carbon atom. This result in a double bond formation between the oxygen and carbon atom. This is because of the electron cloud being transferred from the oxygen. This, there is a possibility of forming the double bond and getting stabilized subsequently. There are a number of electrophilic substitution reactions carried out by the phenols. They are as follows: Kolbe’s reaction. The kolbe’s reaction involves the reaction of phenol with NaOH and formation of phenoxide ion. This phenoxide ion is further treated with acid. This leads to the electrophilic substitution process, and the end product is Salicylic acid. Reimer Tiemann reaction. This reaction involves the treating of phenol compound with chloroform($CHCl_3$) along with base (KOH). The end product formed by subsequent electrophilic substitution reaction is salicylaldehyde. In the above reaction if we may use $CHCl_4$ instead of $CHCl_3$ then the final product obtained will be salicylic acid. Nitration of phenols. Nutrition of phenols involves the electrophilic substitution reaction. When the phenols are reacted with conc. HNO_3 acid then the phenol compound gets substituted with NO_2 at 2, 4, 6 carbon atom of the aromatic ring. Thus, the final product is 2,4,6 trinitrophenol. In order to get mono substituted phenol, we must use dil. HNO_3 acid. Bromination of phenol. The monobromination of phenol can be done by the reaction of Bromine along with non polar solvents like CS_2 or CCl_4. The final product is a monobromo phenol.