

I'm not a robot



Mechanism of reimer tiemann reaction with ccl4

I'd like to expand on Waylander's explanation by focusing on some key points he overlooked, particularly regarding the behavior of CO_2 and how it affects the reactions between phenol and other substances. I'll break down each step using the same starting materials as in the original question. First, let's consider the Reimer-Tiemann reaction: The ethoxide ion acts as a strong base that can abstract an acidic proton from both the phenol and bromochloroiodomethane (CHBrICl), forming a carbanion. This intermediate then releases the iodide ion, resulting in the formation of relatively stable bromochlorocarbene ($\text{FClC}\text{:}$) within the reaction mixture. The key step here is that this carbene serves as an active nucleophile that reacts with the phenoxide anion to produce an anionic intermediate where the charge shifts to the halogenated carbon atom. Following that, a crucial tautomerism occurs from the keto-form of the corresponding phenol to its enol-form in order to achieve aromaticity. This process is thermodynamically driven but plays a critical role as it allows for the transfer of a deuterium ion (D^+) between two centers: either the dihalocarbon or the phenolic oxygen. Since the phenoxide ion is more stable than the carbanion, a 1,2- D^+ shift takes place, resulting in a thermodynamically more stable intermediate where deuterium resides on the dihalocarbon (CBrClD). Subsequently, bromine replacement by a water molecule and rearrangement lead to the formation of the intended deuterated 2-hydroxybenzaldehyde product. It's essential to note that during this reaction, deuterium is not lost but rather transformed into its desired position. Now, let's examine the Kolbe-Schmidt reaction: In this scenario, the hydroxide ion acts as a strong base capable of abstracting an acidic proton from either phenol or chloroform (CHCl_3). However, our starting material is dibromodiodomethane (CBr_2I_2), which lacks acidic hydrogen but can act as an excellent electrophile. Thus, the phenoxide anion generated by reacting with hydroxide ion replaces one iodide ion in CBr_2I_2 to form a neutral trihalo-intermediate. Similar to the previous case, this intermediate represents the keto-form of the corresponding phenol. The subsequent tautomerism from keto- to enol-form is again thermodynamically driven but plays a key role as it affects the behavior of the deuterium ion (D^+). Unlike in the Reimer-Tiemann reaction, where deuterium transfer occurred, in this scenario, the D^+ would be abstracted by another hydroxide ion to form the corresponding phenoxide. The iodine of this intermediate is then replaced by a water molecule followed by a rearrangement that leads to the elimination of one bromine and subsequent hydrolysis to produce the benzoic acid. It's worth noting that, in contrast to the Reimer-Tiemann reaction, deuterium is lost during the transformation in the Kolbe-Schmidt reaction. The Reimer-Tiemann reaction isn't influenced by the phenoxide ion's starting formation, but COO^- is created through hydrolysis following the electrophilic substitution of CBr_2I_2 to the phenol. This type of substitution reaction is named after chemists Karl Reimer and Ferdinand Tiemann. It's employed for ortho-formylation in $\text{C}_6\text{H}_5\text{OH}$ (phenols). When treating phenol with CHCl_3 and NaOH , an aldehyde group (-CHO) is introduced at the ortho position, forming ortho-hydroxybenzaldehyde, known as the Reimer-Tiemann reaction. A common example is converting phenol to salicylaldehyde through this process. Intermediate dichloromethyl-substituted phenol undergoes basic hydrolysis to produce ortho-hydroxybenzaldehyde. The Reimer-Tiemann reaction mechanism involves the formation of a carbene from chloroform, which reacts with phenoxide to form an ortho-formylated product. The reaction is driven by the electron-deficient nature of the carbene and its strong attraction to phenoxide. The Reimer-Tiemann reaction is a type of substitution reaction that produces phenolic aldehydes through the action of chloroform and a strong alkali on phenol. It is an aromatic substitution reaction with significant industrial importance. The mechanism involves several steps, including the formation of dichlorocarbene from chloroform, which reacts with phenoxide to form a C-C double bond. The internal proton is transferred, and release of a chloride ion forms the product. Hydroxide adds to it, releasing the last chloride ion, resulting in tautomerization and the final product. The reaction is also known as the ortho-formylation of phenols using chloroform and NaOH . The intermediate form substituted benzyl chloride is hydrolysed with alkali to supply salicylaldehyde as a product. Due to two main reasons, the Reimer-Tiemann reaction is effective: H-bonding in the final salicylaldehyde and a probability factor. The conditions for this reaction require a biphasic solvent system, which consists of an immiscible mixture of natural and aqueous phases. Phase transfer catalysts or 1,4-Dioxane can facilitate rapid mixing, making the process more efficient. This method is particularly useful with other hydroxy-aromatic compounds like naphthols, requiring heat to initiate the reaction. Once started, it becomes highly exothermic. The mechanism of Reimer-Tiemann involves the deprotonation of chloroform by an aqueous hydroxide solution, forming a chloroform carbanion that readily undergoes alpha-elimination to produce dichlorocarbene. The phenol reactant is then deprotonated by NaOH (aq), creating a negatively charged phenoxide that attacks the dichlorocarbene, forming an intermediate carbene. This intermediate subsequently undergoes hydrolysis to form ortho-hydroxybenzaldehyde. The reaction's specificity towards ortho-formylation arises from the electron-deficient nature of dichlorocarbene due to its two chlorine groups and its strong attraction to phenoxide ions rich in electrons. The Reimer-Tiemann reaction is often modified to produce phenolic acids, such as 2-hydroxybenzoic acid, by substituting chloroform with carbon tetrachloride. Applications of the Reimer-Tiemann reaction include ortho-formylation of phenols, which can be challenging due to its specificity and reactivity. It offers a safe method for direct formylation under non-acidic or anhydrous conditions, making it a preferred choice for aromatic compounds. Furthermore, this reaction is versatile and can accommodate various functional groups, including naphthols, pyrroles, and indoles. The direct formylation of aromatic compounds is predominantly achieved through various methods, including the Gattermann reaction, Gattermann-Koch reaction, Vilsmeier-Haack reaction, and Duff reaction. However, the Reimer-Tiemann reaction stands out as the most advantageous and safe option in chemical synthesis due to its ease of preparation and lack of acidic or anhydrous conditions. Among these reactions, the Reimer-Tiemann reaction is particularly noteworthy for being the most effective path forward. In contrast, the Gattermann-Koch reaction is not applicable to phenol substrates. Key points to note include: - The primary use of organic chemical reactions lies in preparing salicylaldehyde from phenol through a substitution reaction. - In Reimer-Tiemann and Tiemann reactions, reactants involve phenol, CHCl_3 , alkali, and phenol, CCl_4 , alkali. - When phenol, Chloroform, and alkali are used, the product is salicylaldehyde; when phenol, CCl_4 , and alkali are used, the product is salicylic acid. Notable aspects of these reactions include: (i) The formation of a phenoxide ion exhibits both mesomeric and inductive effects, potentially leading to reaction at ortho/para positions. However, due to the decrease in +I effect with increasing distance, the incoming electrophile tends to attack the ortho position. (ii) Simple alkyl groups like methyl or primary alkyl groups react via the SN_2 mechanism, whereas the $\text{S}_{\text{N}}\text{Ar}$ pathway is unstable due to the formation of unstable cations. Conclusion: The Reimer-Tiemann reaction is an example of an electrophilic substitution reaction involving the treatment of phenol with chloroform in NaOH (aq) solution, followed by acid hydrolysis to produce salicylaldehyde. Piperic acid synthesis: Unexpected RT mechanism unlikely: The product obtained was then heated with acetic anhydride and sodium acetate to yield piperic acid, which aligns more closely with expectations than a Reimer-Tiemann (RT) reaction. Given the starting reagents, it is difficult to imagine how an RT-like reaction would occur. However, H. Vyhlídka's work (Chem. Rev. 1960, 60(2), pp 169-184) discusses the first step from catechol to 2,4-dihydroxybenzenecarbaldehyde via an RT reaction. The second step involves diiodomethane to form the acetal, which is also supported by the formation of a similar acetal with 2,4-dihydroxybenzenecarbaldehyde. While further evidence is lacking for the proposed mechanism, it would be suspicious if catechol did not undergo a similar reaction, given its known formation of an acetal with 2,4-dihydroxybenzenecarbaldehyde.