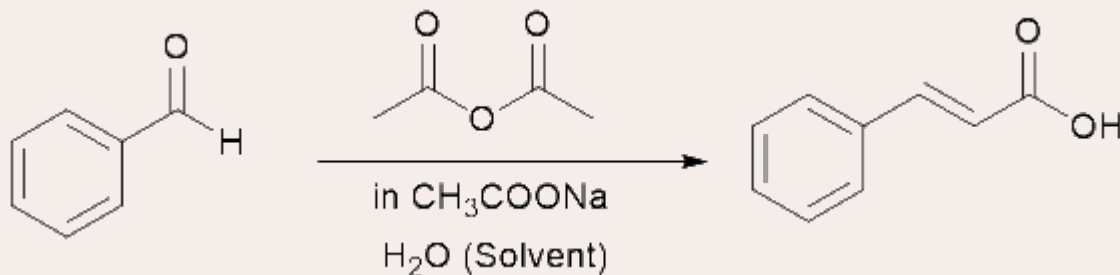


Almonds, Cinnamon, and everything in between

Elementary Problem 7 - 10 points

Deadline: 10th September, 8:30 PM IST

In the 19th Century or early 20th century, when there were no advanced Spectroscopic techniques available, Chemists only used to depend on reaction outcomes and isotopic studies to decipher the plausible mechanisms. One of such reactions whose probable mechanism can be deciphered through these ways is the well-known *Perkin Reaction*. The reaction scheme is provided below for a molecule of Benzaldehyde as the substrate and Acetic Anhydride in Sodium Acetate being the reagent. The reaction is carried in an aqueous solvent and it generates Cinnamic Acid as the end product.



This reaction is one of the C-C bond forming reactions, hence it's believed that the initial step of the reaction occurs through the attack of the carbanion of the anhydride used, generated *in situ*, at the Carbonyl carbon of the aldehyde. However, there can be various pathways that can lead to the final product from the initial step. They are listed as follows,

- **Mechanism A:**

Elimination of a water molecule after the initial attack to generate a double bond followed by hydrolysis to generate the corresponding acid.

- **Mechanism B:**

Acyl transfer to the hydroxyl moiety via a six-membered cyclic intermediate after the initial attack. Then a molecule of acid is eliminated to generate a double bond followed by protonation to generate the corresponding acid.

- **Mechanism C:**

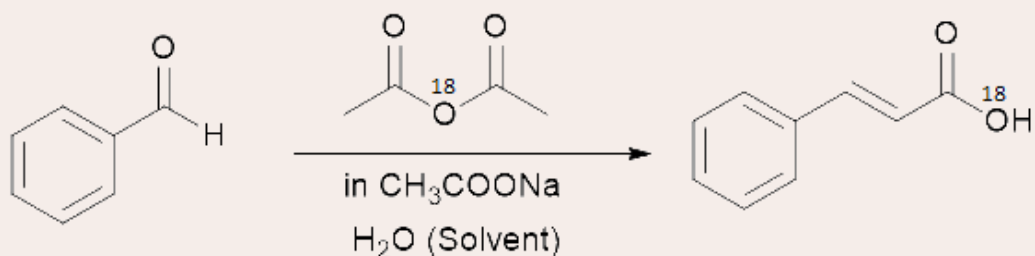
Formation of a four-membered cyclic Wittig type intermediate after the initial stage. At the next step, abstraction of a proton breaking the cyclic structure followed by protonation to generate the acid.

The three mechanisms thus been listed above, the job boils down to find out the one which supports all the experimental evidence. The questions below will help you out to reach the correct mechanism based on some simple experimental results.

1. When isotopically labelled water (H_2O^{18}) was used as the solvent, no isotopically labelled oxygen was found to be present in the Cinnamic Acid. Based on this observation, which mechanism(s) can be rejected out of the three mentioned above. Justify your answer with proper explanation.

(For simplicity, assume that no exchange occurs between the initial reactants and reagents with the solvent).

2. To further investigate, instead of normal Acetic Anhydride, isotopically labelled molecules of Acetic Anhydride are used, the following result was obtained.



Based on this particular observation, which mechanism(s) can be rejected. Justify your answer with proper explanation.

(Again, for simplicity, assume that no exchange occurs within the initial reactants and reagents).

3. Combining the above two results, which of the three can be most suitable mechanism? Write out the steps of the corresponding mechanism.
4. Assuming the mechanism deduced from the previous three questions to be the correct one, what should be the outcome for the following set of reagents ?

