Question #61060 – Chemistry – Organic Chemistry

Questions:

a) Explain the following with suitable examples.

i) Aldehyde without α - hydrogen does not undergo Cannizzaro reaction.

ii) Aldehyde must contain α - hydrogen for aldol condensation.

iii) For Michael addition electron withdrawing group must be present with carbon – carbon double bond.

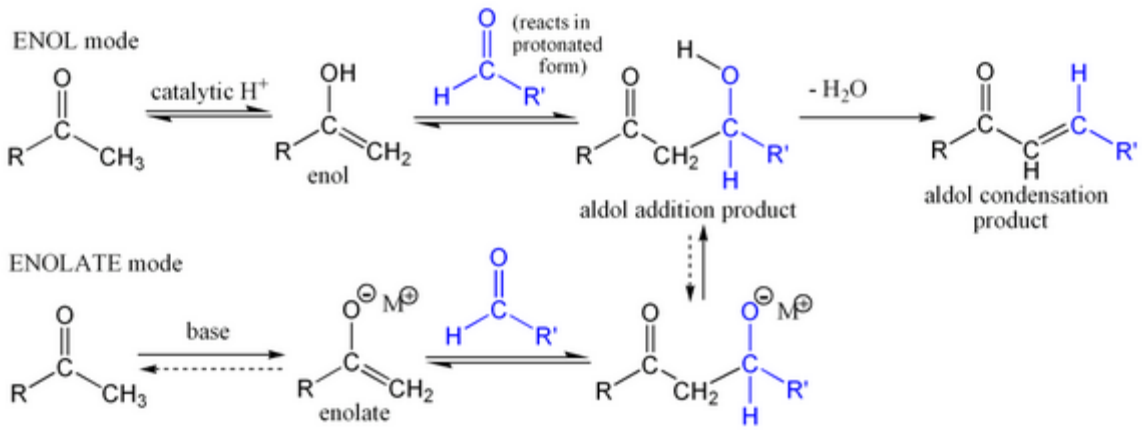
iv) Electron withdrawing substituents at carbonyl carbon increases its reactivity towards nucleophilic addition reactions.

v) Reaction of primary amine, in presence of an acid, with carbonyl compound given an imine. The rate of reaction increases by an increase in acidity but beyond a certain limit, the rate decreases with further increase of acidity.

Answers:

i) Statement is not correct – Correct statement - Aldehyde without α - hydrogen undergoes Cannizzaro reaction

ii) Enol should be formed in time of aldol condensation. It is formed only if aldehyde has a-hydrogen.

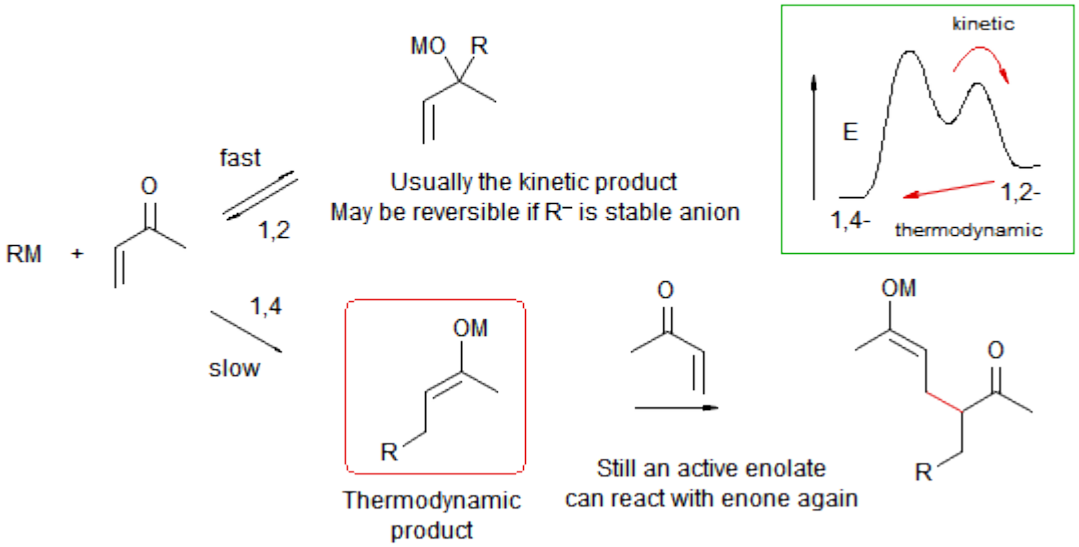


iii) Two process should occur when nucleophile attac a,b-unsatured aldehyde – 1,2- and 1,4-addition. 1,4 addition is preferable when double bound is chear on electrons – when electron withdrawing group present with carbon – carbon double bond.
Also problem that product of Michael addition can react with starting aldehyde as result big amount of undesired products is formed.This problem can be solved if activity of centers in product molecules will be reduced by electron withdrawing group.

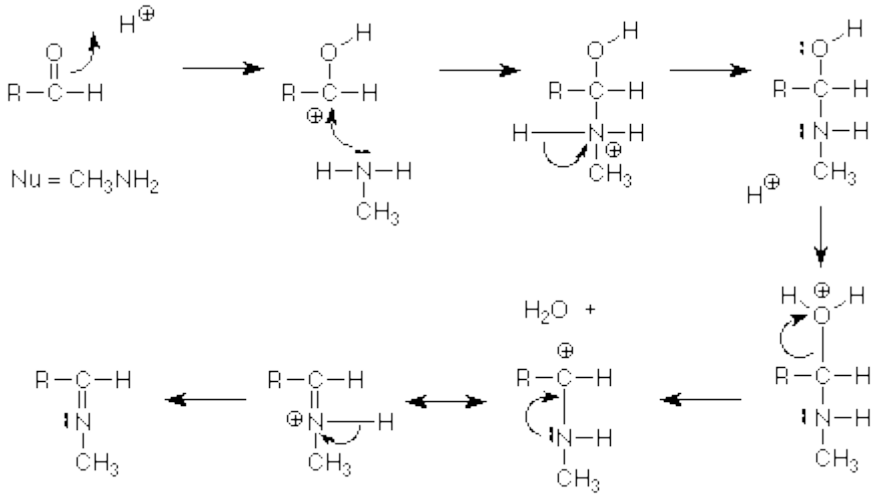
Major problems:

1. 1,2 vs 1,4 addition
2. 1,4 addition product is an active donor

- Relative reactivity of RM and product enolate
- Lifetime of product enolate



iv) Electron withdrawing substituents at carbonyl carbon increases its reactivity towards nucleophilic addition reactions because they increace active positive charge on carbon atom as result nucleofile attacks more easily.



v) On the first step imine attack carbocation – the lower pH the faster first step occur – this stage limits rate of all reaction. But if pH is very low – amine exist inform RNH_3^+ - this is not nucleofile – N does not have electron pair – as result – reactuion occur more slowly.