

Study Notes On The Doebner Modification



The Doebner Modification

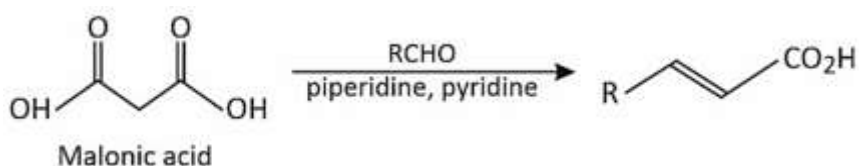
It is an extension to the Knoevenagel reaction.

When one of the electron withdrawing groups on nucleophile is carboxylic acid, i.e., if malonic acid is used in place of active methylene group and it reacts with aldehyde in presence of mild base, the condensation reaction occurs and the product formed undergoes decarboxylation (loss of CO_2) and yields α, β -unsaturated carboxylic acid.

This process is termed as the Doebner modification.

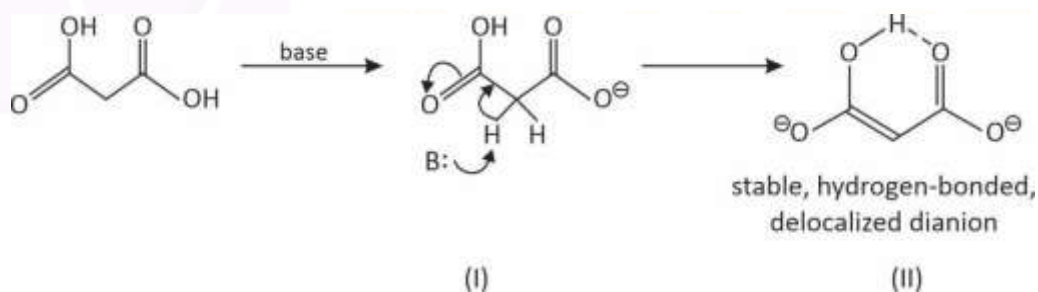
Here, the base used is Pyridine.

General reaction-

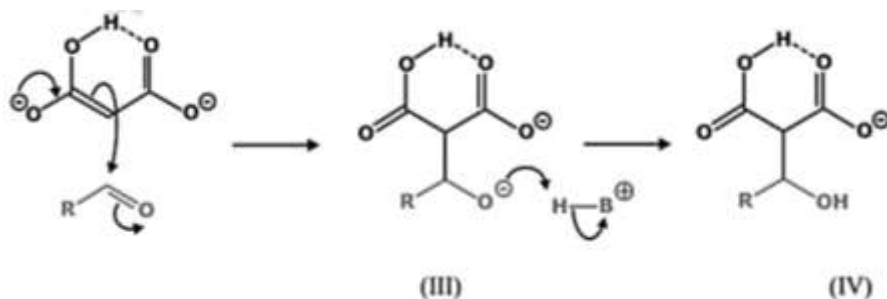


Reaction mechanism-

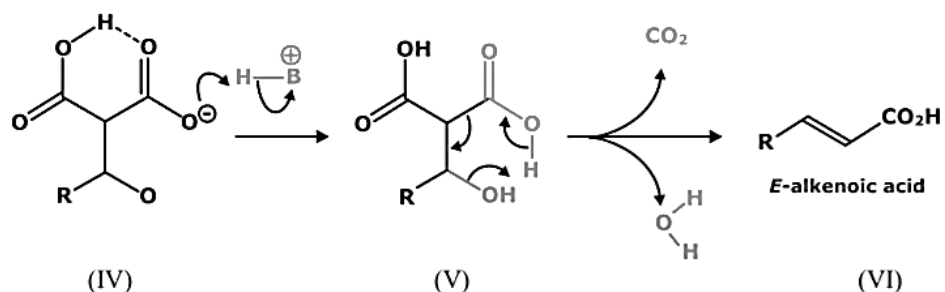
Base abstracts the active methylene hydrogen atom resulting in enolate ion(I). The enolate formed in this case is a dianion and is quite stable due to extensive delocalization and the intramolecular hydrogen bond (II).



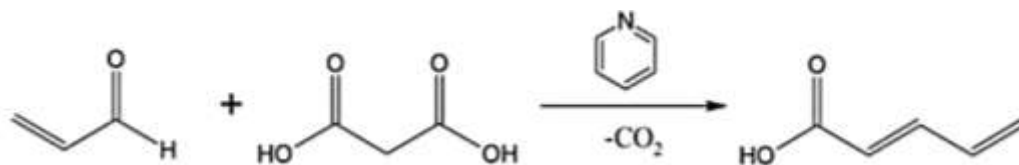
The dianion attacks as nucleophile to the electrophilic carbonyl carbon of the aldehyde, and after proton abstraction from the medium (III), the aldol (IV) is formed (monocarboxylate in this basic solution).



From the aldol (IV), the next step to take place is decarboxylation and dehydration. The decarboxylation and dehydration occur via a cyclic transition state (V). Note that ideally, CO_2 from any of the two $-\text{COOH}$ groups could happen, which could give either E or Z double bond in the product. But since the product has E (or trans) geometry, that transition state is involved which has lower energy leading to more stable E alkenoic acid (VI) as the product.



Example-



The Doebner modification of the Knoevenagel condensation. Acrolein and malonic acid react in pyridine to give trans-2,4-pentadienoic acid with the loss of carbon dioxide

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