

Michael Addition Reaction: The Michael reaction or Michael addition reaction is the nucleophilic addition of a carbanion or nucleophile to an α, β -unsaturated carbonyl compound containing the electron withdrawing group.

It is a conjugate addition reaction and useful method for C-C bond formation. e.g



α, β -unsaturated carbonyl compounds are often known as Michael acceptor

Nucleophile or Michael donor	Michael acceptor	Product
Cyanide	$\text{KCN} + \text{CH}_2=\text{CH}-\text{C}(=\text{O})\text{OMe}$	$\text{NC}-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})\text{OMe}$
Amines	$\text{Et}_2\text{NH} + \text{CH}_2=\text{CH}-\text{C}(=\text{O})\text{OEt}$	$\text{Et}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})\text{OEt}$
Alcohols	$\text{MeOH} + \text{CH}_2=\text{CH}-\text{CHO}$	$\text{Me}-\text{CH}_2-\text{CH}_2-\text{CHO}$
Thiols	$\text{MeSH} + \text{CH}_2=\text{CH}-\text{CHO}$	$\text{MeS}-\text{CH}_2-\text{CH}_2-\text{CHO}$
Bromides	$\text{HBr} + \text{CH}_2=\text{CH}-\text{CHO}$	$\text{Br}-\text{CH}_2-\text{CH}_2-\text{CHO}$
Chloride	$\text{HCl} + \text{CH}_2=\text{CH}-\text{CHO}$	$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{CHO}$
Benzene	$\text{C}_6\text{H}_6 + \text{CH}_2=\text{CH}-\text{COOH}$	$\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\text{COOH}$

Michael donor: Michael donor include

Malonic ester, cyanoacetic ester, acetoacetic ester,

Phenylacetic acid ester

Cyanoacetamide

Aliphatic Nitro compounds

Benzyl cyanide, Sulphones, Cyclopentadienes, indenes, Fluorenes etc.

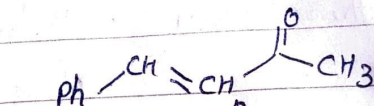
Michael Acceptors: a) α, β -unsaturated aldehydes

e.g. acrolein $\text{CH}_2=\text{CH}-\text{CHO}$

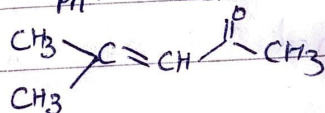
Cinnamaldehyde $\text{Ph}-\text{CH}=\text{CH}-\text{CHO}$

b) α, β -unsaturated ketones

e.g. benzylidene acetone

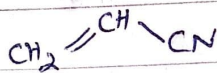


Mesityl oxide



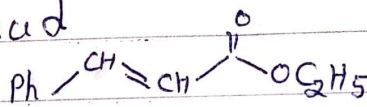
c) α, β -unsaturated nitriles

e.g. acrylonitrile



d) Ester of α, β -unsaturated acid

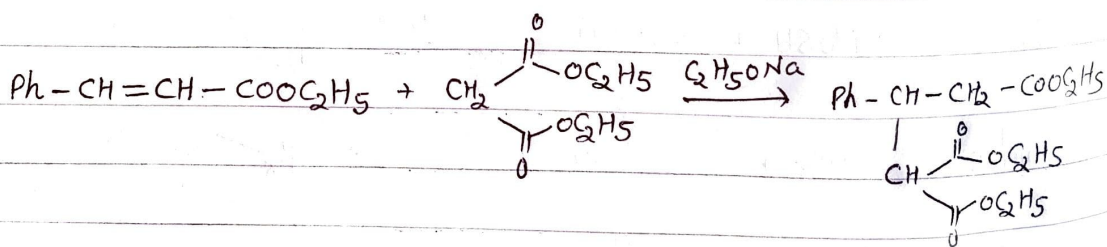
e.g.



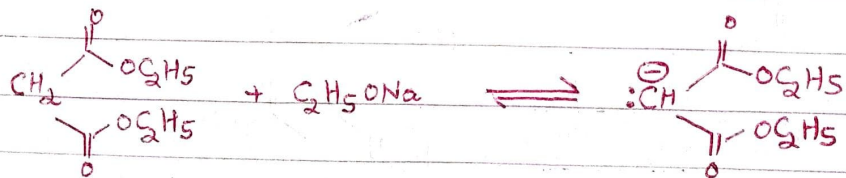
Since it is a base catalysed reaction. Most commonly used bases are alkali metal alkoxide such as sodium or potassium ethoxide, potassium tertiary butoxide, potassium isopropoxide etc.

Mild basic catalyst such as 2° amines, 3° amine, piperidine and pyridine have been used for the success of the reaction.

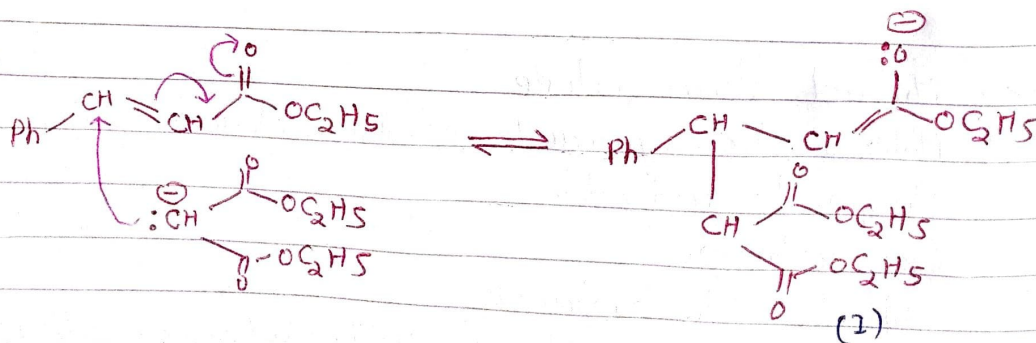
Mechanism

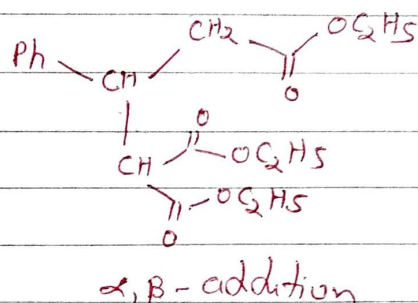
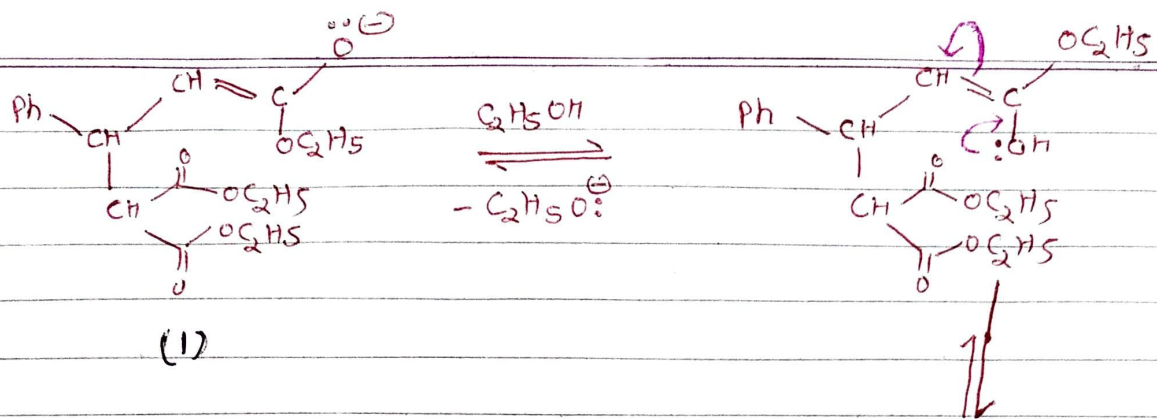


Step 1 →



Step 2 →





* In the first step, base generates a carbanion from the donor i.e. Malonic ester

* In second step, carbanion attack on the β -carbon of α, β -unsaturated ester acceptor (Ethyl cinnamate) to yield the anion (I), which takes a proton from the alcohol to produce the enol. The enol then tautomerises to the more stable product ketone.

Note: * Electron withdrawing group - COOC_2H_5 (or Z) facilitates the attack by stabilizing the intermediate anion (I) by dispersal of charge.

* Although 1,4-addition seems to occur initially, the final result is the addition to the α, β -unsaturated carbon. This is because the enol reverts to the more stable ketone.

* In the presence of strong base, the product may undergo cyclisation, but no cyclisation occurs with the mild base such as 2° or 3° amines and piperidine.