

③ CO-VALENT CATALYSIS

A catalyst that adds to substrate through co-valent bond is known as covalent catalyst. The phenomenon is known as covalent catalysis.

e.g ① Electrophilic catalysis by Schiff base formation -

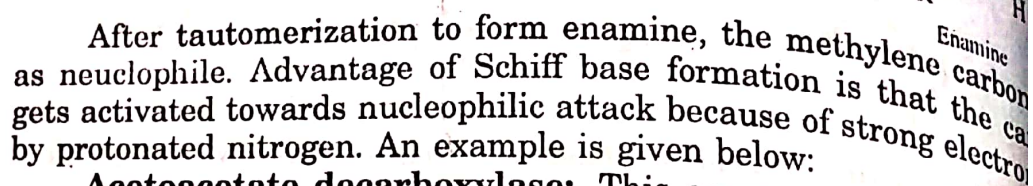
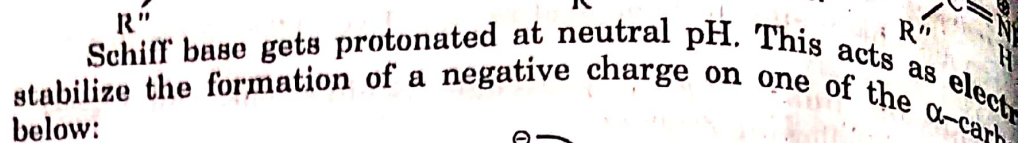
② Pyridoxal phosphate - Electrophilic catalysis -

③ Thiamine pyrophosphate (Electrophilic catalysis -

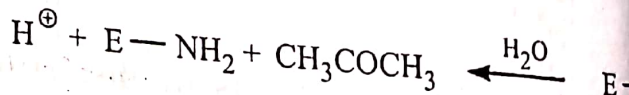
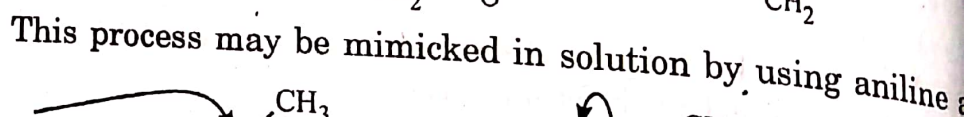
④ Nucleophilic catalysis -

December	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F	S	S	2006					
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24				25	26	27

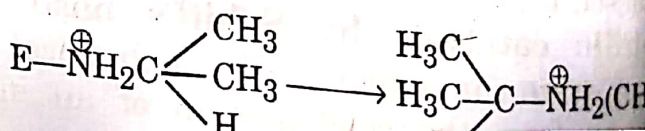
2006

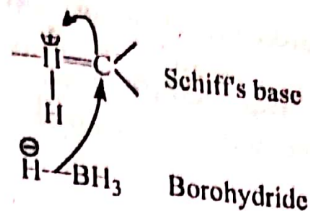


Acetoacetate decarboxylase: This enzyme catalyses decarboxylation of acetoacetate. The nonenzymatic reaction involves the expulsion of enolate ion at neutral pH, but the enzymatic reaction circumvents formation of a Schiff base with lysine residue. The protonated enolate is readily expelled.



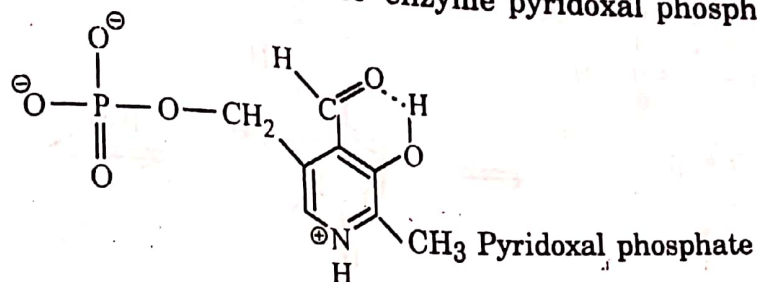
The evidence for intermediate is that the enzyme is irreversible when sodium borohydride is added to complex with the substrate. It is known to reduce Schiff bases, and the hydrolysate of the inhibitor is found to contain isopropyl-lysine. The carbon in the Schiff base is attacked by an H^{\ominus} ion from the borohydride:



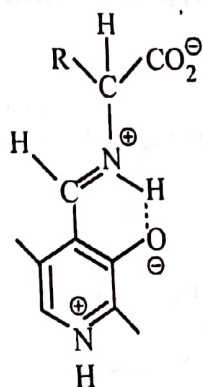


2. Pyridoxal phosphate—Electrophilic catalysis

The principles discussed above form the basis of a series of important metabolic interconversions involving the co-enzyme pyridoxal phosphate.

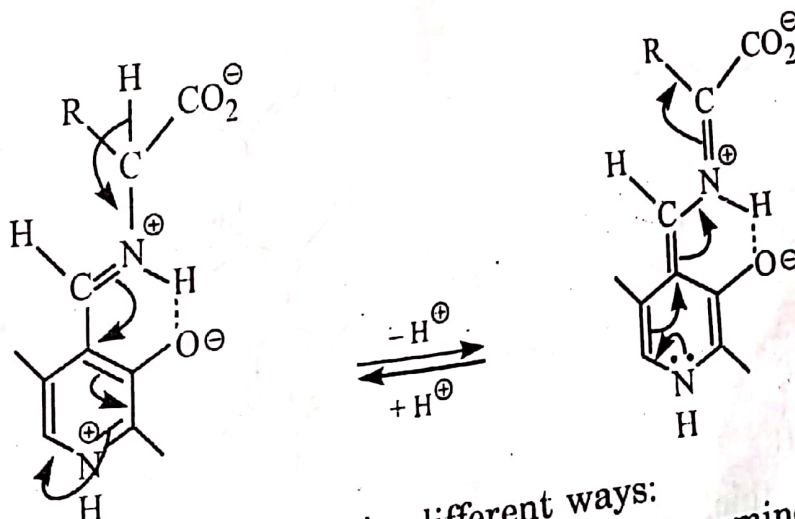


This condenses with amino acids to form a Schiff base. The pyridine ring in the Schiff base acts as an "electron sink" which very effectively stabilizes a negative charge:



Each of the groups around the chiral carbon of amino acid may be cleaved forming an anion that is stabilized by the Schiff base with the pyridine ring. Different processes involved are discussed below:

(a) **Removal of α -hydrogen:** The removal of the α -hydrogen gives a k intermediate.



This intermediate may react in different ways:
Removal of proton back to amino acid will lead