α,β-Unsaturated Carbonyl Compounds:*

In general, a compound that contains both a **carbon-carbon double bond and a carbon-oxygen double bond** has properties that are characteristic of both functional groups.

At the **carbon-carbon double bond** an unsaturated ester or unsaturated ketone undergoes electrophilic addition of acids and halogens, hydrogenation, hydroxylation, and cleavage;

at the **carbonyl group** it undergoes the nucleophilic substitution typical of an ester or the nucleophilic addition typical of a ketone.
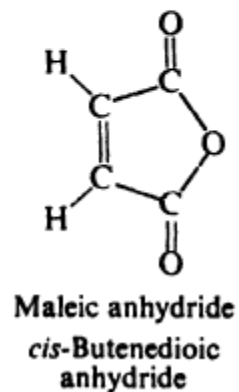
$$\overset{\beta}{-C}=\overset{\alpha}{C}-C=O$$

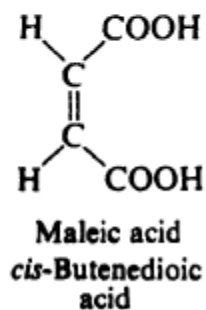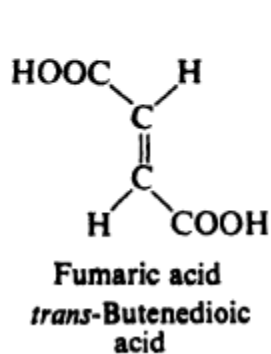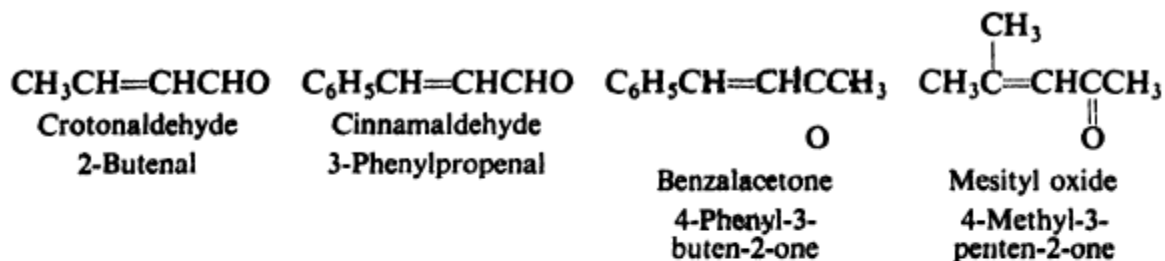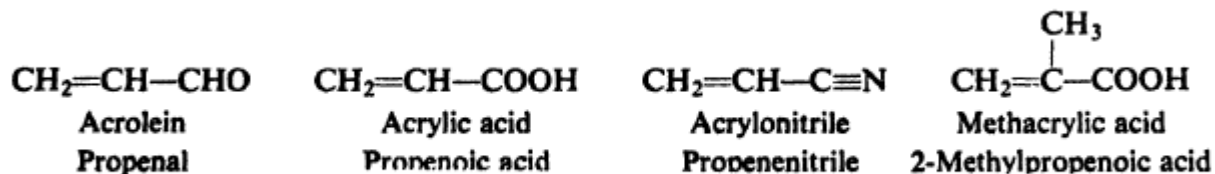**α,β-Unsaturated carbonyl compound**
Conjugated system
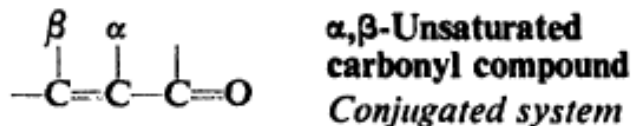
As a result of conjugation, such compounds possess not only the properties of the individual functional groups, but certain other properties besides. In this chapter we shall concentrate on the α,β-unsaturated compounds, and on the special reactions characteristic of the conjugated system.

Examples of α,β-Unsaturated Carbonyl Compounds

Name	Formula	M.p., °C	B.p., °C
Acrolein	$CH_2\!=\!CHCHO$	− 88	52
Crotonaldehyde	$CH_3CH\!=\!CHCHO$	− 69	104
Cinnamaldehyde	$C_6H_5CH\!=\!CHCHO$	− 7	254
Mesityl oxide	$(CH_3)_2C\!=\!CHCOCH_3$	42	131
Benzalacetone	$C_6H_5CH\!=\!CHCOCH_3$	42	261
Dibenzalacetone	$C_6H_5CH\!=\!CHCOCH\!=\!CHC_6H_5$	113	.
Benzalacetophenone (Chalcone)	$C_6H_5CH\!=\!CHCOC_6H_5$	62	348
Dypnone	$C_6H_5C(CH_3)\!=\!CHCOC_6H_5$		150–5[1]
Acrylic acid	$CH_2\!=\!CHCOOH$	12	142
Crotonic acid	trans-$CH_3CH\!=\!CHCOOH$	72	189
Isocrotonic acid	cis-$CH_3CH\!=\!CHCOOH$	16	172d
Methacrylic acid	$CH_2\!=\!C(CH_3)COOH$	16	162
Sorbic acid	$CH_3CH\!=\!CHCH\!=\!CHCOOH$	134	
Cinnamic acid	trans-$C_6H_5CH\!=\!CHCOOH$	137	300
Maleic acid	cis-$HOOCCH\!=\!CHCOOH$	130.5	
Fumaric acid	trans-$HOOCCH\!=\!CHCOOH$	302	
Maleic anhydride		60	202
Methyl acrylate	$CH_2\!=\!CHCOOCH_3$		80
Methyl methacrylate	$CH_2\!=\!C(CH_3)COOCH_3$		101
Ethyl cinnamate	$C_6H_5CH\!=\!CHCOOC_2H_5$	12	271
Acrylonitrile	$CH_2\!=\!CH\!-\!C\!\equiv\!N$	− 82	79

$CH_2\!=\!CH\!-\!CHO$
Acrolein
Propenal

$CH_2\!=\!CH\!-\!COOH$
Acrylic acid
Propenoic acid

$CH_2\!=\!CH\!-\!C\!\equiv\!N$
Acrylonitrile
Propenenitrile

$CH_2\!=\!\overset{CH_3}{\underset{|}{C}}\!-\!COOH$
Methacrylic acid
2-Methylpropenoic acid

$CH_3CH\!=\!CHCHO$
Crotonaldehyde
2-Butenal

$C_6H_5CH\!=\!CHCHO$
Cinnamaldehyde
3-Phenylpropenal

$C_6H_5CH\!=\!CHCCH_3$
$\overset{\|}{O}$
Benzalacetone
4-Phenyl-3-buten-2-one

$CH_3\overset{CH_3}{\underset{|}{C}}\!=\!CHCCH_3$
$\overset{\|}{O}$
Mesityl oxide
4-Methyl-3-penten-2-one

Fumaric acid
trans-Butenedioic acid

Maleic acid
cis-Butenedioic acid

Maleic anhydride
cis-Butenedioic anhydride

Preparation:

There are several general ways to make compounds of this kind: the **aldol condensation**, to make unsaturated **aldehydes and ketones** ; **dehydrohalogenation of α-halo acids** and the **Perkin condensation**, to make **unsaturated acids**.

Interaction of functional groups:

Electrophilic Addition

$$-\overset{|}{C}=\overset{|}{C}-G + Y^+ \longrightarrow \left[-\overset{|}{C}\overset{...}{=}\overset{|}{C}-G \atop \underset{Y\,\delta_+}{\overset{\delta_+}{\downarrow}} \right] \longrightarrow -\overset{|}{\underset{\underset{Y}{\downarrow}}{C}}-\overset{|}{C}-G \overset{\oplus}{}$$

G releases electrons: activates
G withdraws electrons: deactivates
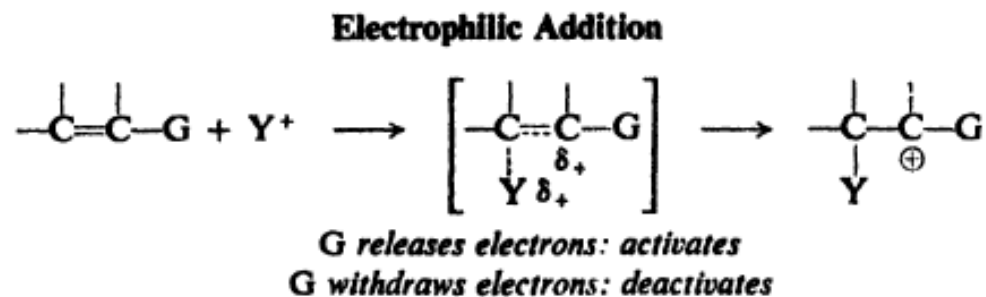
The C=O, COOH, COOR, and CN groups are powerful electronwithdrawing groups, and therefore would be expected to deactivate a carboncarbon double bond toward electrophilic addition.
This is found to be true: α, β-unsaturated ketones, acids, esters, and nitriles are in general less reactive than simple alkenes toward reagents like bromine and the hydrogen halides.

But this powerful electron withdrawal, which deactivates a carbon-carbon double bond toward reagents seeking electrons, at the same time activates toward reagents that are electron-rich.
As a result, the carbon-carbon double bond of an α,β-unsaturated ketone, acid, ester, or nitrile is susceptible to nucleophilic attack, and undergoes a set of reactions, nucleophilic addition, that is uncommon for the simple alkenes.

Electrophilic addition:

The presence of the carbonyl group not only lowers the reactivity of the carbon-carbon double bond toward electrophilic addition, but also controls the orientation of the addition.

In general, it is observed that addition of an unsymmetrical reagent to an α,β-unsaturated carbonyl compound takes place in such a way that hydrogen becomes attached to the a-carbon and the negative group becomes attached to the β-carbon. For example:

$$CH_2{=}CH{-}CHO + HCl(g) \xrightarrow{-10°} \underset{\underset{Cl \quad H}{|\quad|}}{CH_2{-}CH{-}CHO}$$

Acrolein   β-Chloropropionaldehyde

$$CH_2{=}CH{-}COOH + H_2O \xrightarrow{H_2SO_4,\ 100°} \underset{\underset{OH \quad H}{|\quad|}}{CH_2{-}CH{-}COOH}$$

Acrylic acid   β-Hydroxypropionic acid

$$CH_3{-}CH{=}CH{-}COOH + HBr(g) \xrightarrow{20°} \underset{\underset{Br \quad H}{|\quad|}}{CH_3{-}CH{-}CH{-}COOH}$$

Crotonic acid   β-Bromobutyric acid

$$\underset{\underset{O}{\|}}{\underset{|}{\overset{CH_3}{\overset{|}{CH_3{-}C{=}CH{-}C{-}CH_3}}}} + CH_3OH \xrightarrow{H_2SO_4} \underset{\underset{CH_3O \quad H \quad O}{|\qquad|\quad\|}}{\overset{CH_3}{\overset{|}{CH_3{-}C{-}CH{-}C{-}CH_3}}}$$

Mesityl oxide   4-Methoxy-4-methyl-2-pentanone

Electrophilic addition to simple alkenes takes place in such a way as to form the most stable intermediate carbocation. Addition to α,β-unsaturated carbonyl compounds, too, is consistent with this principle; to see that this is so, however, we must look at the conjugated system as a whole.

Addition to the carbonyl oxygen end would yield carbocation I; addition to the β-cairbon end would yield carbocation II.
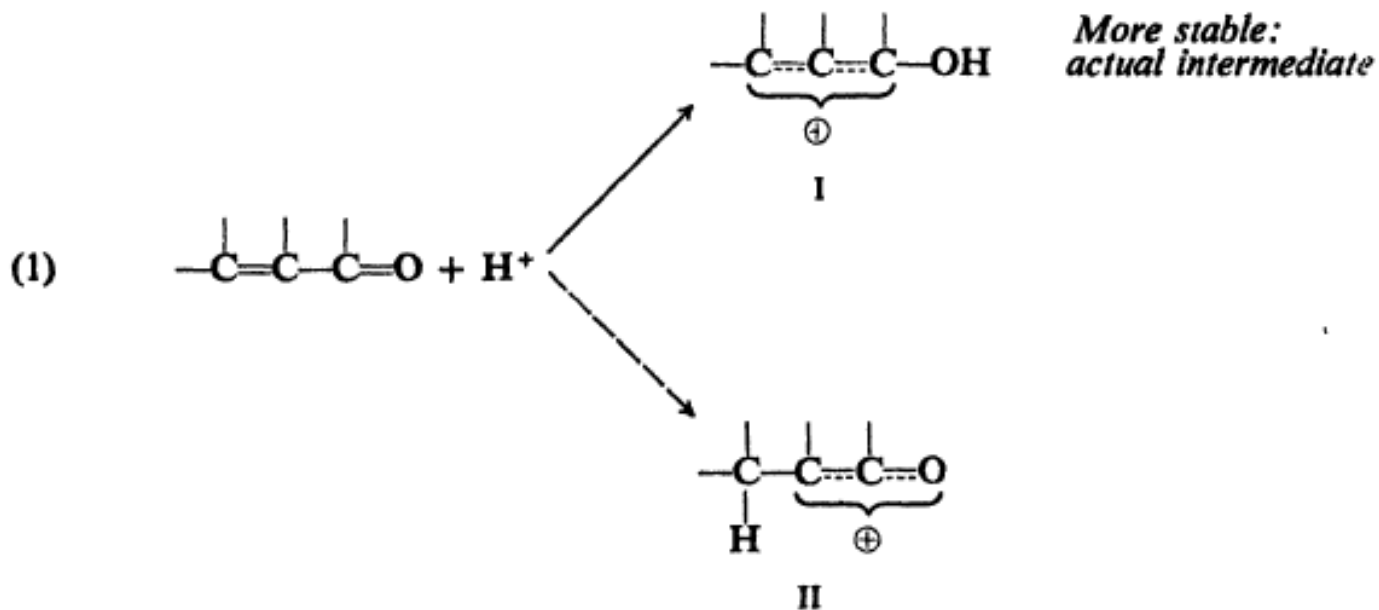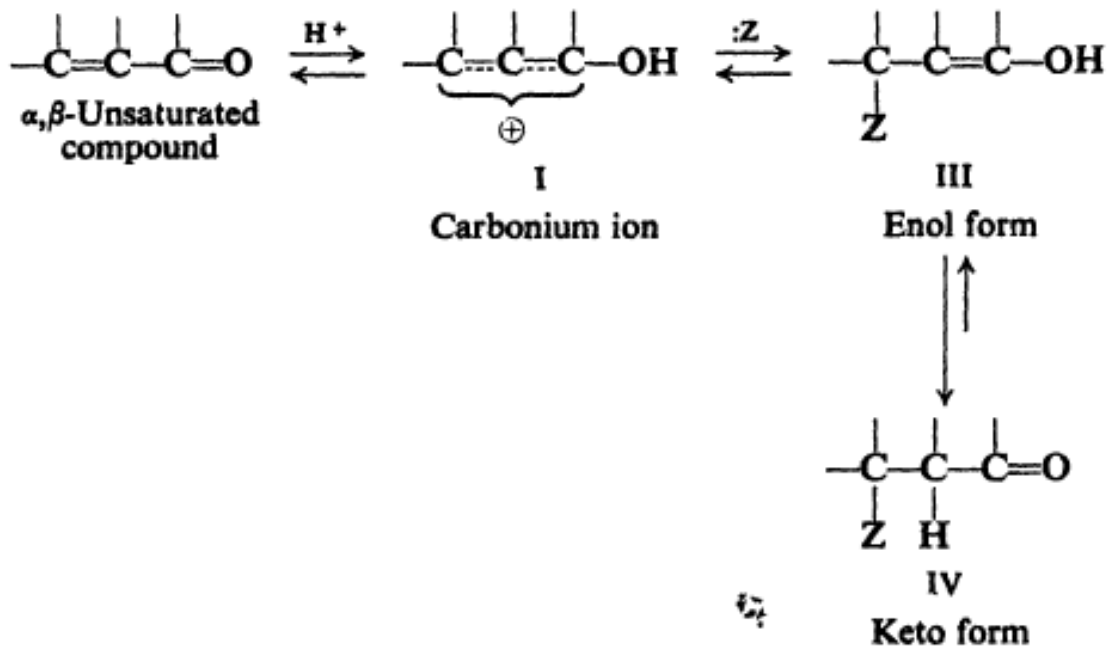
Of the two, I is the more stable, since the positive charge is carried by carbon atoms alone, rather than partly by the highly electronegative oxygen atom.

In the second step of addition, a negative ion or basic molecule attaches itself either to the carbonyl carbon or to the ,β-carbon of the hybrid ion I.
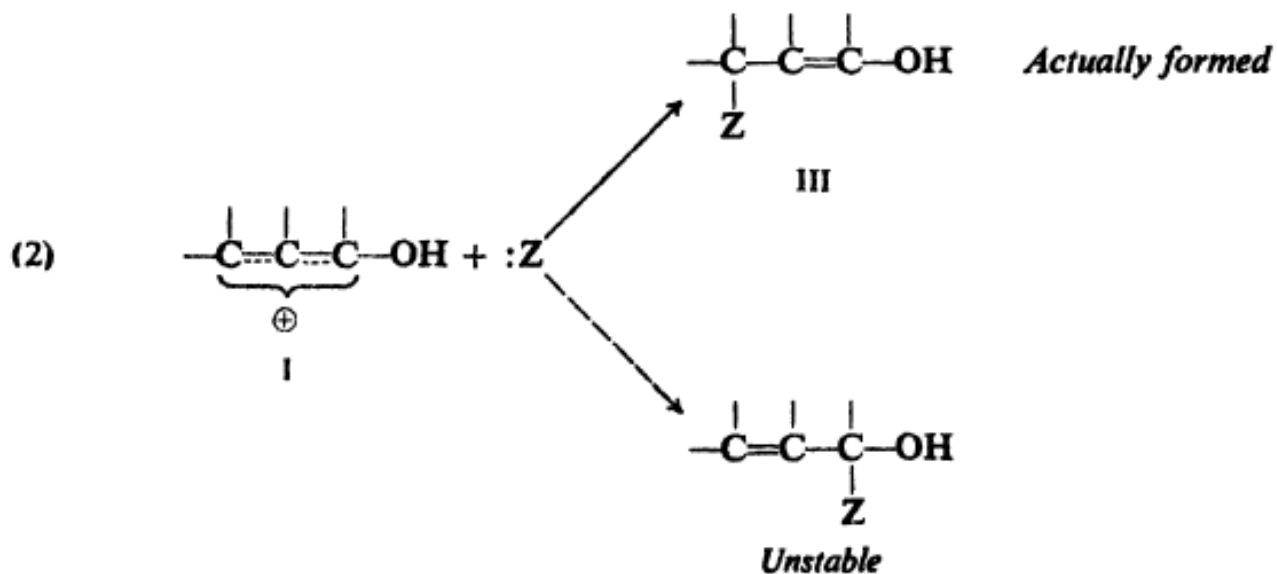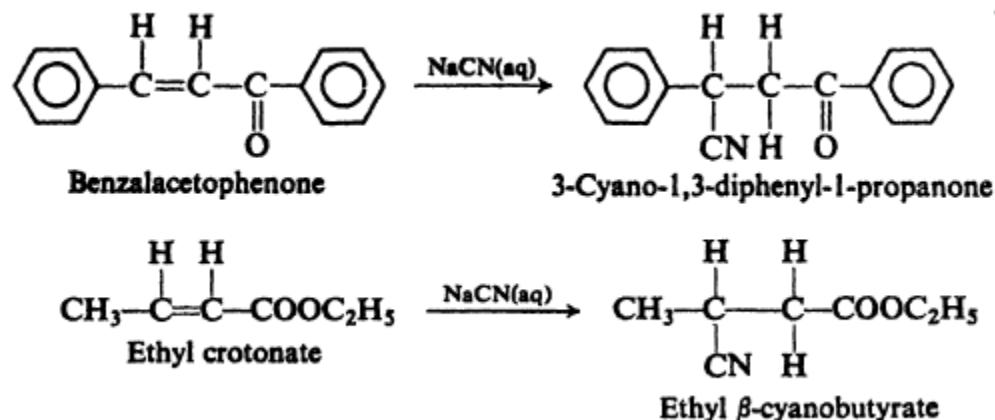
Of the two possibilities, only addition to the β-carbon yields a stable product (III), which is simply the enol form of the saturated carbonyl compound. The enol form then undergoes tautomerization to the keto form to give the observed product (IV).
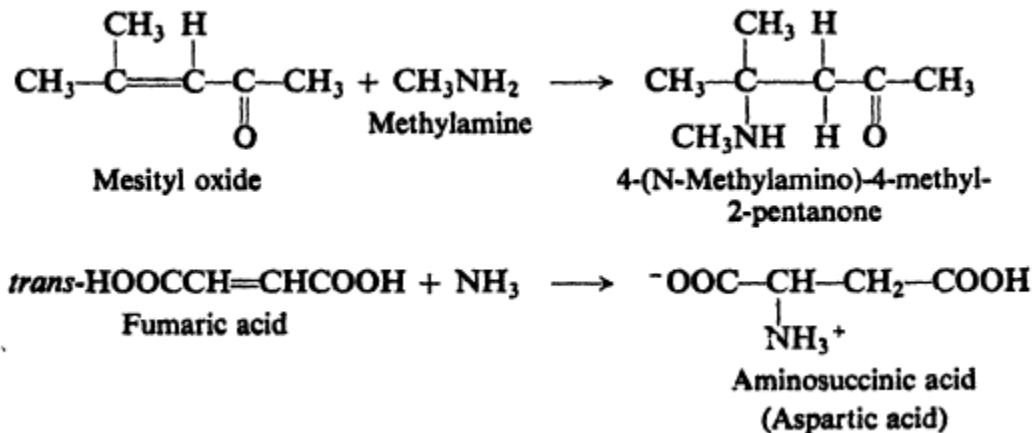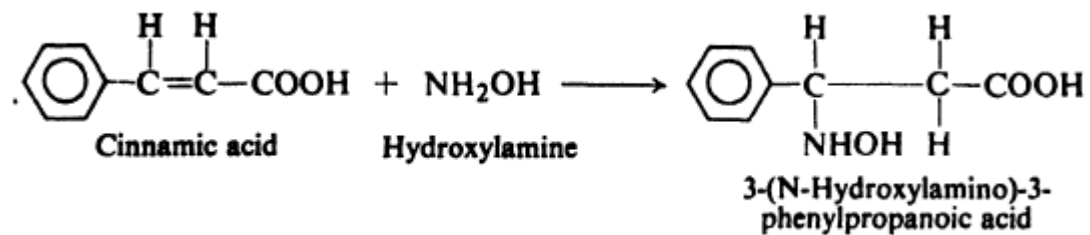
$$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O \underset{}{\overset{H^+}{\rightleftharpoons}} -\overset{|}{C}\cdots\overset{|}{C}\cdots\overset{|}{C}-OH \underset{}{\overset{:Z}{\rightleftharpoons}} -\overset{|}{\underset{|}{C}}-\overset{|}{C}=\overset{|}{C}-OH$$

α,β-Unsaturated compound

⊕

I

Carbonium ion

III

Enol form

$$-\overset{|}{\underset{Z}{C}}-\overset{|}{\underset{H}{C}}-\overset{|}{C}=O$$

IV

Keto form

Nucleophilic addition:

Aqueous sodium cyanide converts α,β-unsaturated carbonyl compounds into β-cyano carbonyl compounds. The reaction amounts to addition of the elements of HCN to the carbon-carbon double bond. For example:
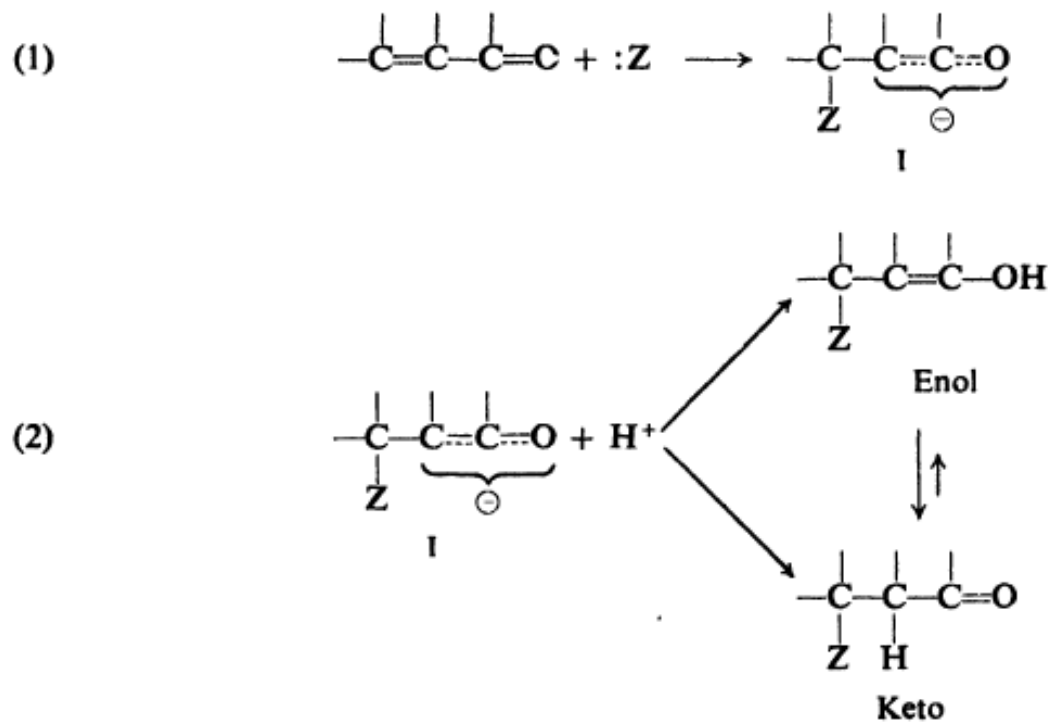

Benzalacetophenone → 3-Cyano-1,3-diphenyl-1-propanone

Ethyl crotonate → Ethyl β-cyanobutyrate

Ammonia or certain derivatives of ammonia (amines, hydroxylamine, phenylhydrazine, etc.) add to α,β-unsaturated carbonyl compounds to yield β-amino carbonyl compounds. For example:


Mesityl oxide + Methylamine → 4-(N-Methylamino)-4-methyl-2-pentanone

trans-HOOCCH=CHCOOH + NH₃ → ⁻OOC—CH—CH₂—COOH

Fumaric acid → Aminosuccinic acid (Aspartic acid)

Cinnamic acid + Hydroxylamine → 3-(N-Hydroxylamino)-3-phenylpropanoic acid

These reactions are believed to take place by the following mechanism:
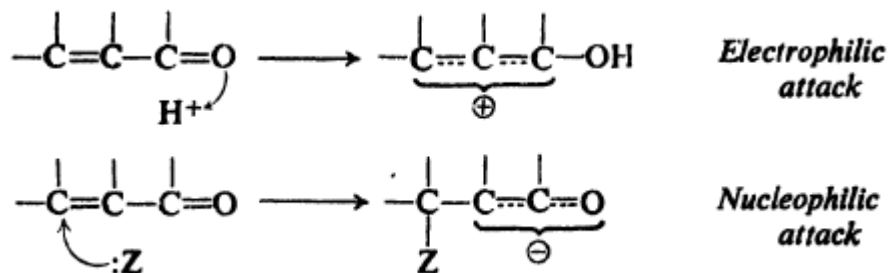
(1)

(2)

Enol

Keto

The nuclecphilic reagent adds (step 1) to the carbon-carbon double bond to yield the hybrid anion I, which then accepts (step 2) a hydrogen ion from the solvent to yield the final product. This hydrogen ion can add either to the α-carbon or to oxygen, and thus yield either the keto or the enol form of the product; in either case the same equilibrium mixture, chiefly keto, is finally obtained.
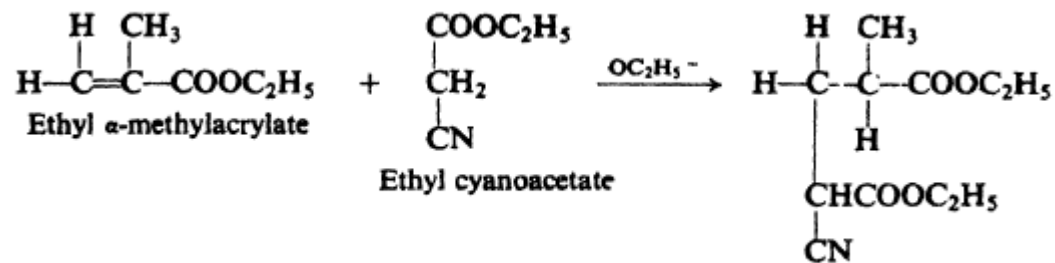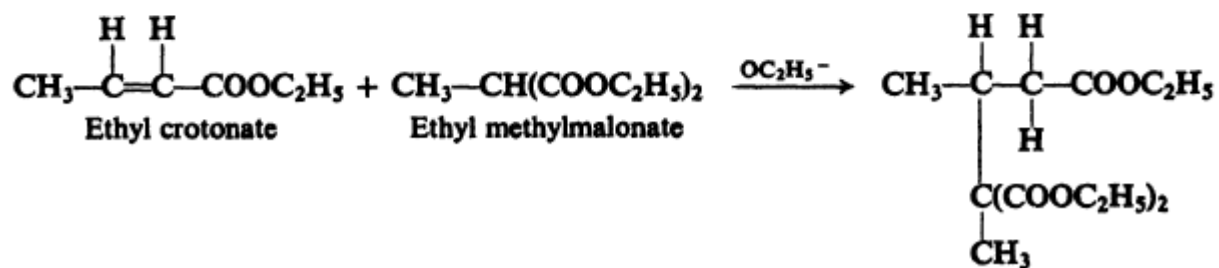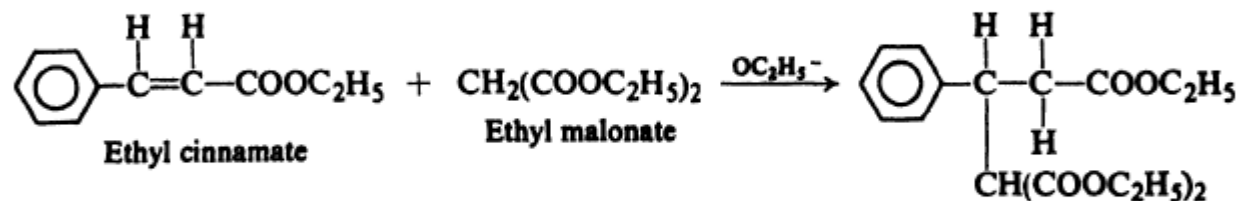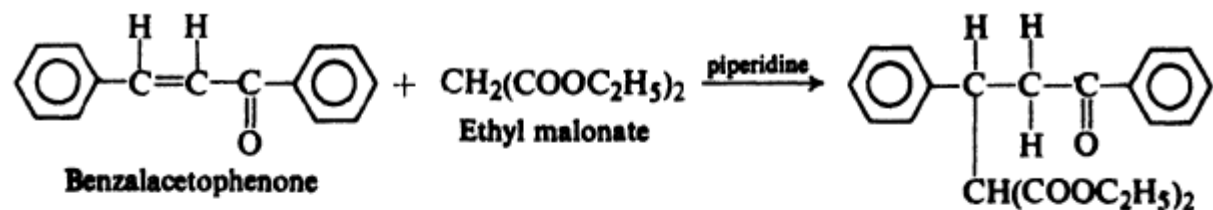
The nucleophilic reagent add to the conjugated system in such a way as to form the most stable intermediate anion. The most stable anion is I, which is the hybrid of II and III.
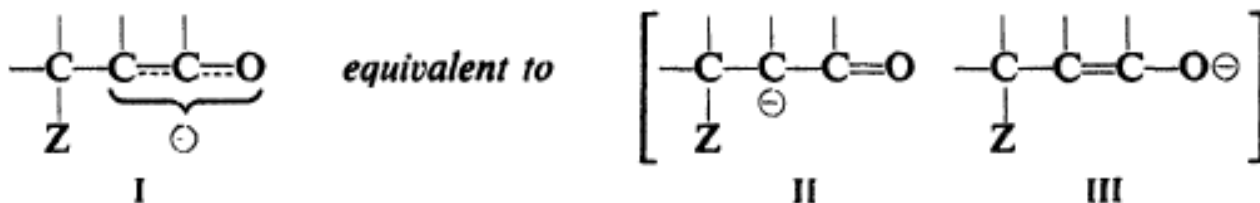
Difference between nucleophilic and electrophilic addition

The Michael addition:

The mechanism:

(1) $\quad CH_2(COOC_2H_5)_2 + :Base \longrightarrow H:Base^+ + CH(COOC_2H_5)_2$

(2) $\quad$ $-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O + CH(COOC_2H_5)_2{}^- \longrightarrow$

Nucleophilic reagent

(3) $\quad$ $-\overset{|}{C}-\overset{|}{C}\!\!=\!\!\overset{|}{C}\!\!=\!\!O + H:Base^+ \longrightarrow -\overset{|}{C}-\overset{|}{C}-\overset{|}{C}=O + :Base$