3) α,β-Unsaturated carbonyl compounds:

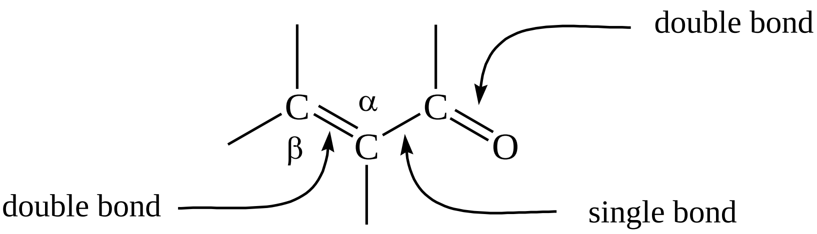
3:1) Structure and properties:

In general , a compound that contain both of carbon – carbon double bond and carbon – oxygen double bond has properties that characteristic of both functional groups .

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

At the carbonyl group it undergoes nucleophilic substitution typical of an ester or nucleophilic addition typical of a ketone .

In these compounds, the carbon – carbon double bond and the carbon – oxygen double bond are separated by just one carbon – carbon single bond; that is the double bonds are conjugated.



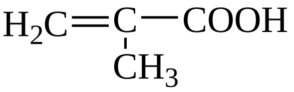
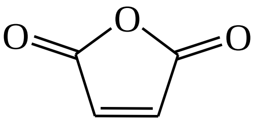
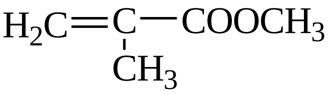
α,β-Unsaturated carbonyl compounds
(conjugated system)

Because of this conjugation, such compounds possess not only the properties of the individual functional groups, but certain properties besides.

So we shall concentrate on the α,β-unsaturated carbonyl compounds, and on the special reactions characteristic of the conjugated system.

The following table lists some of the most important compounds of this type:

Compound name	**Structure**
Acroline (propenal)	$H_2C{=}CHCHO$
Crotonaldehyde (2- butenal)	$H_3CHC{=}CHCHO$
Cinnamaldehyde	$PhHC{=}CHCHO$
Mesityl oxide	$(H_3C)_2C{=}CHCOCH_3$

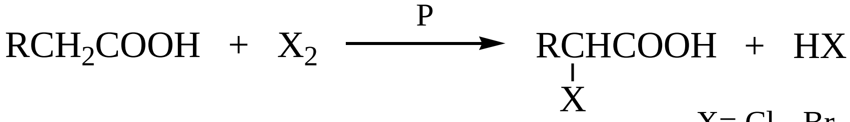
Benzalacetone	$PhHC{=}CHCOCH_3$
Dibenzalacetone	$PhHC{=}CHCOCH{=}CHPh$
Bezalacetophenone (chalcone)	$PhHC{=}CHCOPh$
Dypnone	$Ph(H_3C)C{=}CHCOPh$
Acrylic acid (propenoic acid)	$H_2C{=}CHCOOH$
Crotonic acid	trans- $H_3CHC{=}CHCOOH$
Isocrotonic acid	cis- $H_3CHC{=}CHCOOH$
Methacrylic acid	 $H_2C{=}\underset{CH_3}{\underset{\vert}{C}}{-}COOH$
Sorbic acid	$H_3CHC{=}CHCH{=}CHCOOH$
Cinnamic acid	trans- $PhHC{=}CHCOOH$
Maleic acid	cis- $HOOCHC{=}CHCOOH$
Fumaric acid	trans- $HOOCHC{=}CHCOOH$
Maleic anhydride	
Methyl acrylate	$H_2C{=}CHCOOCH_3$
Methyl methacrylate	 $H_2C{=}\underset{CH_3}{\underset{\vert}{C}}{-}COOCH_3$
Ethyl cinnamate	$PhHC{=}CHCOOC_2H_5$
Acrylonitrile	$H_2C{=}CHC{\equiv}N$

3:2) Preparation:

These compounds have been synthesized by different methods like:

1- The aldol condensation to make unsaturated aldehydes or ketones.
2- Dehydrohalogenation of α-halo acids. (α-halo acids prepared by halogenation of unsubstituted acids, which known as Hell-Volhard-Zelinsky).

e.g. for H.V.Z. reaction:



$$RCH_2COOH + X_2 \xrightarrow{P} \underset{X}{\underset{\vert}{R}}CHCOOH + HX$$

$X= Cl_2, Br_2$

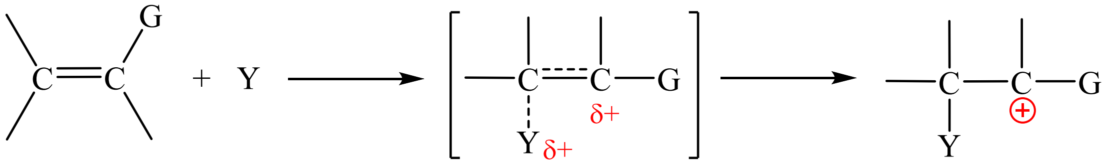
3- Perkin condensation.

Note: *Methods 2 and 3 used to make unsaturated acids. Other methods can be used for making single compounds.*

3:3) Interaction of functional groups:

As we know, electrophilic addition on carbon – carbon double bond is activated by an electron – releasing substituent (EDG) and deactivated by an electron – withdrawing substituent (EWG).

Hint: *(the carbon – carbon double bond serve as a source of electrons for electrophilic reagents; the availability of its electrons is determined by the group that attached to it. Moreover EDGs stabilizes the T.S. leading to the initial carbocation by dispersing the +ve charge, this in contrast with EWGs which destabilize the T.S.by intensifying the +ve charge).*



If G is an EDG $\Longrightarrow$ activates
If G is an EWG $\Longrightarrow$ deactivates

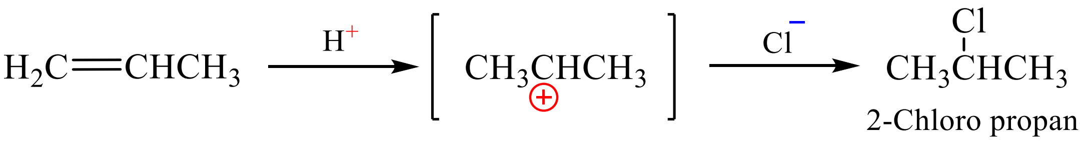
The C=O, COOH, COOR and CN groups are powerful electron withdrawing groups, and therefore deactivate the C=C toward electrophilic addition, thus α,β-unsaturated ketones, acids, esters or nitriles are in general less reactive than simple alkene toward reagents like bromine and hydrogen halides.

On the other hand this powerful electron withdrawal, which deactivate 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 ketones, acids, esters or nitriles is susceptible to nucleophilic attack, and undergoes a set of reactions, nucleophilic addition, that is uncommon for simple alkenes.

3:4) Electrophilic addition:

In general, the addition of an unsymmetrical reagent (E^+) to simple alkenes takes place in such a way that form the most stable intermediate carbocation.

e.g.

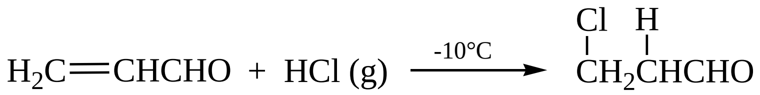


$$H_2C{=}CHCH_3 \xrightarrow{H^+} \left[CH_3\underset{\oplus}{C}HCH_3 \right] \xrightarrow{Cl^-} CH_3\overset{Cl}{C}HCH_3$$

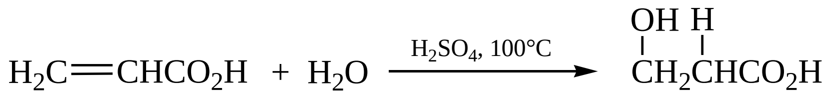
2-Chloro propane

The presence of carbonyl group not only lowers the reactivity of the carbon – carbon double bond toward electrophilic addition, but also control the orientation of the addition, thus addition of an electrophile to an α,β-unsaturated carbonyl compound proceed in such a way that hydrogen becomes attached to the α- carbon and the negative group attached to the β- carbon.

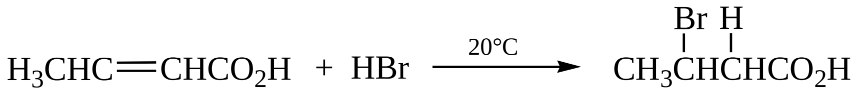
e.g.

1)

$H_2C{=}CHCHO + HCl\,(g) \xrightarrow{-10°C} \overset{Cl}{CH_2}\overset{H}{C}HCHO$

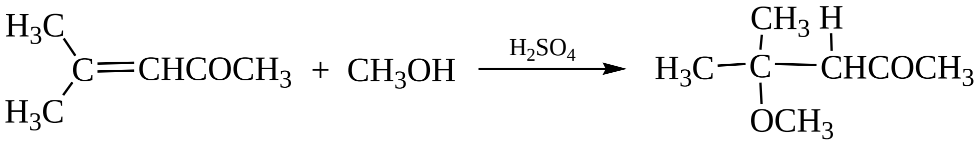
Acroline β- Chloro propionaldehyde

2)

$H_2C{=}CHCO_2H + H_2O \xrightarrow{H_2SO_4,\ 100°C} \overset{OH}{CH_2}\overset{H}{C}HCO_2H$

Acrylic acid β- Hydroxy propionic acid

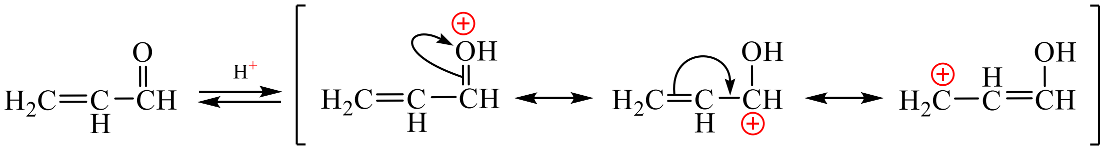
3)

$H_3CHC{=}CHCO_2H + HBr \xrightarrow{20°C} CH_3\overset{Br}{C}H\overset{H}{C}HCO_2H$

Crotonic acid β- Bromo butyric acid

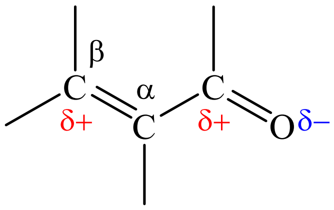
4)


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

The presence of carbonyl group polarize the carbon – carbon double bond, thus addition of an electrophile proceeded as the following:

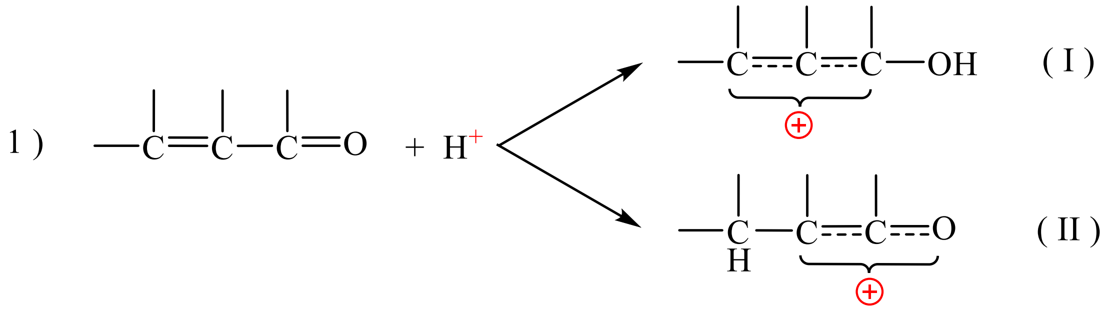


As we can see from the above hybridized structures the β- carbon and the carbonyl carbon bearing a partially positive charge while the carbonyl oxygen bear a partially negative charge:



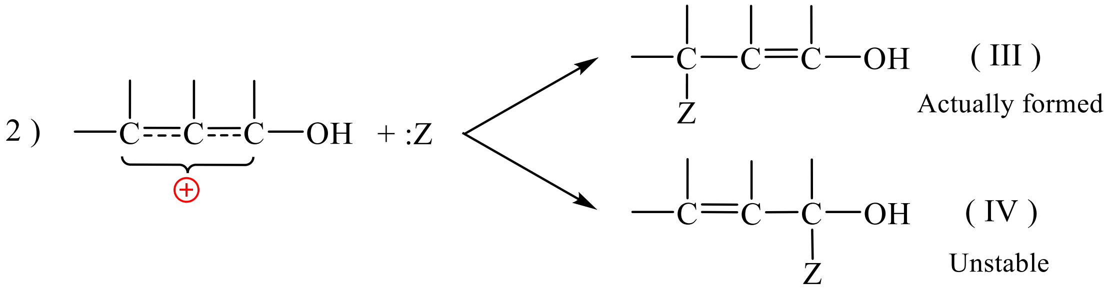
Addition of an electrophile to α,β-unsaturated carbonyl compounds proceed through the formation of more stable carbocation.

Addition can be proceed to either end of the conjugated system taking in our account the stability of the intermediate, thus addition to the carbonyl oxygen end would yield carbocation (I); while addition to the β- carbon end yield carbocation (II).

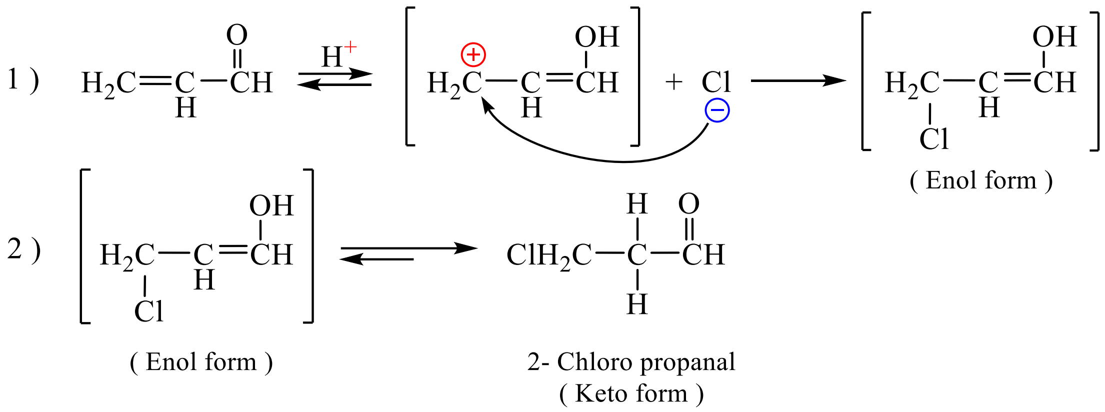


Cation (I) is more stable than cation (II), since the positive charge is carried by carbon atoms alone, rather than partly by the highly electronegative oxygen atom.

In the second step the negative ion or basic molecule attach itself either to the carbonyl carbon or β- carbon of 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, that undergoes tautomerization to the keto form, as we can see from the following scheme of the addition of HCl gas to acroline:



One can ask why doesn’t the nuleophile attack the carbonyl carbon that also bear the positive charge in ion (I) ?

In fact this could be happen, but the product is unstable and convert to the starting material as the following: