Chapter 6 Ketones and Aldehydes

Day – 1

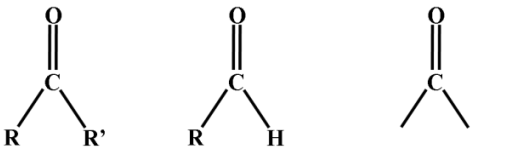
Ketones and Aldehydes

Carbonyl Compounds

We will study compounds containing the carbonyl group (C = O) in detail because they are of central importance to organic chemistry, biochemistry and biology. Some of the common types of carbonyl compounds are listed in table.

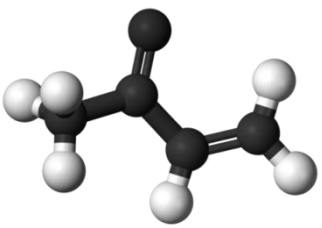
Carbonyl compounds are everywhere. In addition to their uses as reagents and solvents, they are constituents of fabrics, flavorings, plastics and drugs. Naturally occurring carbonyl compounds include proteins, carbohydrates, and nucleic acids that make up all plants and animals. In the next few chapters, we will discuss the properties and reactions of simple carbonyl compounds. Then, in chapter 23 and 24, we apply this carbonyl chemistry to carbohydrates, nucleic acids, and proteins.

The simplest carbonyl compounds are ketones and aldehydes. A ketone has two alkyl (or aryl) group bonded to the carbonyl carbon atom. An aldehyde has one alkyl (or aryl) group and one hydrogen atom bonded to the carbonyl carbon atom.

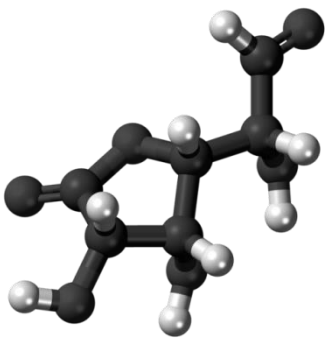


Condensed structure:	Ketone RCOR'	Aldehyde RCHO	Carbonyl group

Ketone:- Two alkyl groups bonded to a carbonyl group.



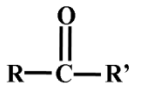
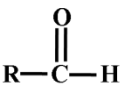
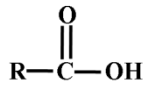
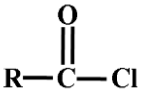
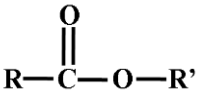
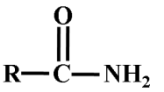
Methyl-vinyl-ketone



Glucuronolactone-(aldehyde)

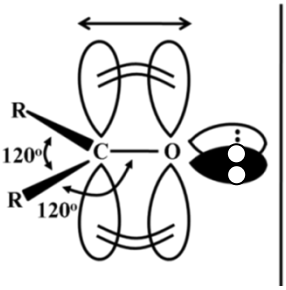
Aldehyde:-One alkyl group and one hydrogen bonded to a carbonyl group.

Ketones and aldehydes are similar in structure, and they have similar properties. There are some differences, however, particularly in their reactions with oxidizing agents and with nucleopiles. In most cases, aldehydes are more reactive then ketones, for reasons we discuss shortly.

Some Common Classes of Carbonyl Compounds			
Class	General Formula	Class	General Formula
Ketones		Aldehydes	
Carboxylic acids		Acid chlorides	
Esters		Amides	

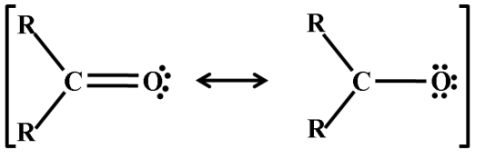
Structure of the Carbonyl Group

The carbonyl carbon atom is sp^2 hybridized and bonded to three other atoms through coplanar sigma bonds oriented about 120° apart. The unhybridized *p* orbital overlaps with a *p* orbital of oxygen to form a pi bond. The double bond between carbon and oxygen is similar to an alkene C = C double bond, except that the carbonyl double bond is shorter, stronger, and polarized.



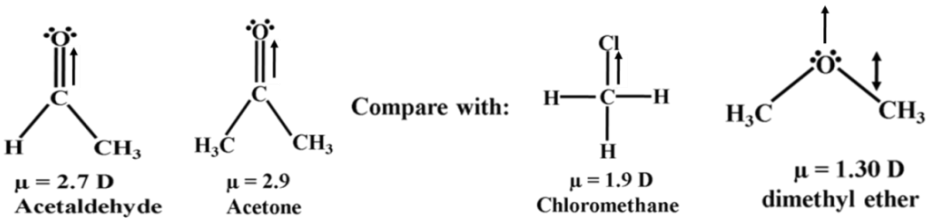
	length	*energy*
ketone C═O bond	1.23 Å	178 kcal/mol (745 kJ/mol)
Alkene C═C bond	1.34 Å	146 kcal/mol (611 kJ/mol)

The double bond of the carbonyl group has a large dipole moment because oxygen is more electronegative then carbon, and the bonding electrons are not shared equally. In particular, the less tightly held pi electrons are pulled more strongly towards the oxygen atom, giving ketones and aldehydes larger dipole moments than most alkyl halides and ethers. We can use resonance forms to symbolize this unequal sharing of the pi electrons.



major **minor**

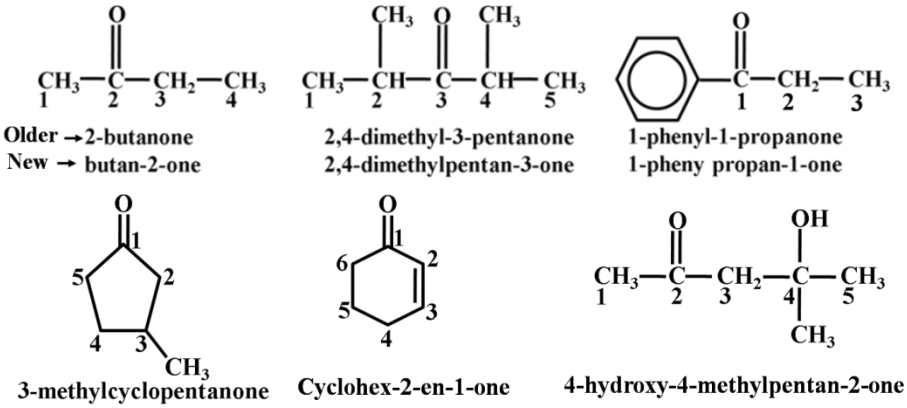
The first resonance form is more important because it involves more bonds and less charye separation. The contribution of the second structure is evidenced shown below.



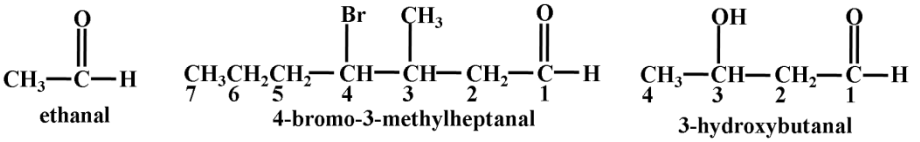
This polarization of the carbonyl group contributes to the reactivity of ketones and aldehydes. The positively polarized carbon atoms acts as an electrophile (Lewis acid), and the negatively polarized oxygen acts as a nucleophile (Lewis base).

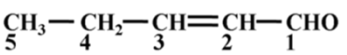
Nomenclature of ketones and Aldehydes

Systematic names of ketones are derived by replacing the final *–e* in alkane name with *–one*. The "alkane" name becomes "alkanone." In open–chain ketones, we number the longest chain that includes the carbonyl carbon from the end closed to the carbonyl group, and we indicate the postion of the carbonyl group by a number. In cyclic ketones, the carbonyl carbon atom is assigned the number 1.

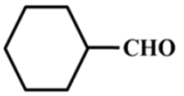


Systematic names for aldehydes are derived by replacing the final –e of the alkane name with *–al*. An aldehyde carbon is at the end of a chain, so it is number 1. If the aldehyde group is attached to a large unit (usually a ring), the suffix –carbaldehyde is used.

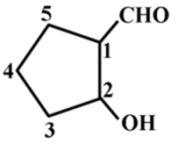




Pent-2-enal

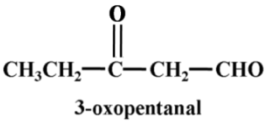


cyclohexanecarbaldehyde

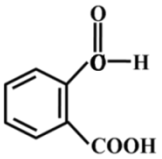


2-hydroxycyclopentane-1-carbaldehyde

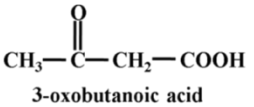
A ketone or aldehyde group can also be named as a substituent on a molecule with another functional group as its root. The ketone carbonyl is designated by the prefix *oxo*-, and the — CHO group is named as a *formyl* group. Carboxylic acids frequently contain ketone or aldehyde groups named as substituents.



3-oxopentanal

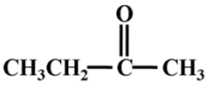


2-formylbenzoic acid



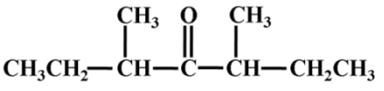
3-oxobutanoic acid

Common Names:- As with other classes of compounds, ketones and aldehydes are often called by common names instead of their systematic IUPAC names. Ketones common names are formed by naming the two alkyl groups bonded to the carbonyl group. Substituent locations are given using Greek letters, beginning with the new the carbonyl group.



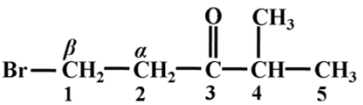
methyl ethyl ketone

IUPAC name : Butan-2-one



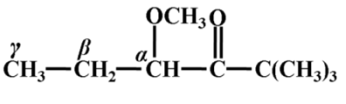
di-*sec*-butyl ketone

3,5-dimethyl heptan-4-one



β -bromoethyl isopropyl ketone

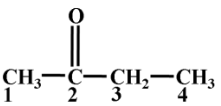
1-bromo-4-methyl pentan-3-one



t-butyl *α* –methoxypropyl ketone

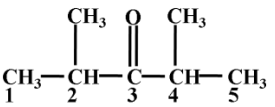
4-methoxy-2, 2-dimethyl hexan-3-one

some ketones have historical common names. Dimethyl ketone is always called acetone, and alkyl phenyl ketones are usually name as the acyl group followed by the suffix –phenone.



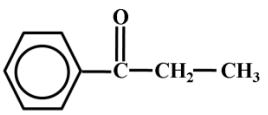
2-butanone

butan-2-one



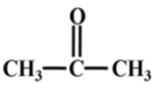
2,4-dimethyl-3-pentanone

2,4-dimethylpentan-3-one

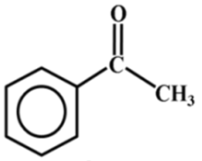


1-phenyl-1-propanone

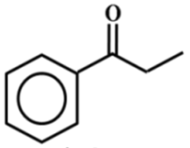
1-pheny propan-1-one



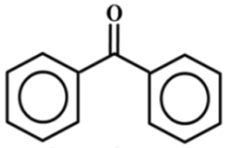
acetone
Propanone



acetophenone
1-phenyl ethanone

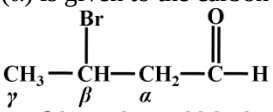


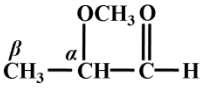
propiophenonoe
1-phenyl propan-1-one



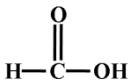
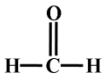
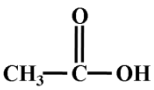
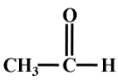
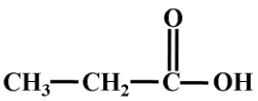
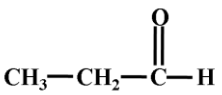
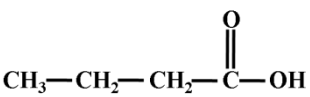
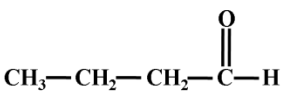
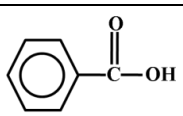
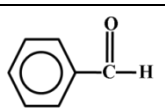
benzophenone
diphenyl methanone

Common names of aldehydes are derived from the common names of carboxylic acids (Table). These names often reflect the Latin or Greek term for the original source of the acid or the aldehyde. Greek letters are used with common names of aldehydes to give the location of substituents. The first letter (α) is given to the carbon atom next to the carbonyl group.

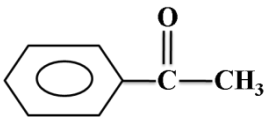
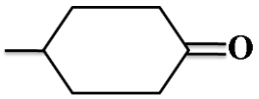
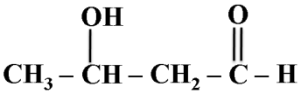
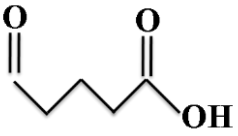
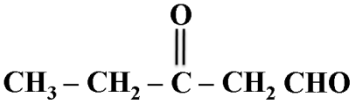
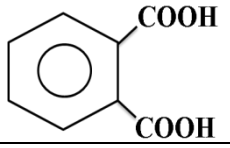
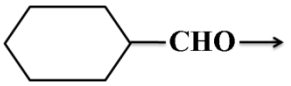
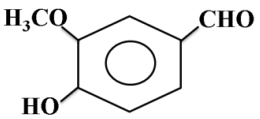
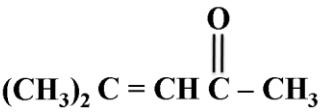


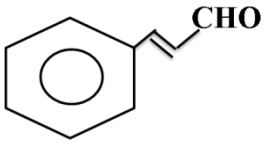
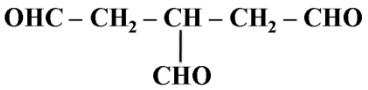


Common name: β-bromobutyraldehyde α-methoxypropionaldehyde
IUPAC name: 3-bromobutanal 2-methoxypropanal

Common Names of Aldehydes		
Carboxylic Acid	**Derivation**	**Aldehyde**
 formic acid	*formica*, "ants"	 formaldehyde (methanal)
 acetic acid	*acetum*, "sour"	 acetaldehyde (ethanal)
 propionic acid	*protos pion*, "first fat"	 propionaldehyde (propanal)
 butyric acid	*butyrum*, "butter"	 butyraldehyde (butanal)
 benzoic acid	*gum benzoin*, "blending"	 benzaldehyde

Nomenclature

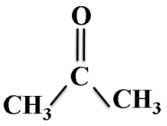
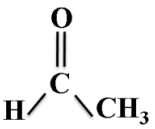
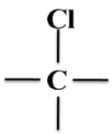
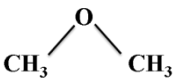
Structure	Common name	IUPAC name
	Aceto-phenone	1-phenylethan-1-one
		4-methylcyclohexanone
		3-hydroxybutanal
		5-oxopentanoicacid
		3-oxopentanal
		2-formyl benzoic acid
		cyclohexanecarbaldehyde
$CH_3CH_2CH_2CHO$	butyraldehyde	butanal
$CH_2 = CH\ CHO$	acrolein	Prop-2-en-l-ol
	Vanillin	4-nhydroxy-3-methoxy benzaldehyde
	mesityloxide	4-methyl pent-3-ene-2-one

	Tr-cinnamaldehyde	(2E)-3-phenyl prop-2-en-1-ol
	3-formyl pentan-1,5-dial	Propane-1,2,3-tricarboldehyde

Physical Properties

	Bond length	**bond energy**
	1.23 A^o	745 KJ/mole
C = C	1.34 A^o	611 KJ/mole

Dipole moment:- High dipole moment

compound				
dipole	2.9 D	2.7 D	1.9 D	1.9 D

Hydrogen bond:-

No H-bond with itself but can form H-bond with water or alcohol. So it is a good solvent.

Formaldehyde:-

Is gas so mixed with water 40% aqueous solution called formalin

Acetaldehyde:- bp 20^o

Acetone:-

Industrial solvent nearly 3 billion kg/year many Aldehydes and Ketones are used as flaouring agent.