

PURE & APPLIED CHEMISTRY

SCH 230: Chemistry of Carbonyl and Organometallic Compounds

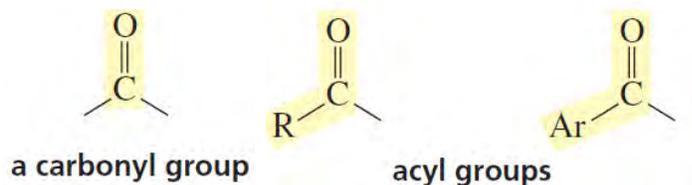
Lecture Notes I

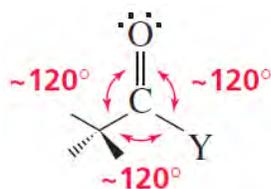
Lecturer: Rahab Kamau (PhD)

Carbonyl Compounds

The **carbonyl group** refers to a carbon double bonded to an oxygen. Compounds containing carbonyl groups are called **carbonyl compounds**. Many such compounds play important roles in biological processes. Hormones, vitamins, amino acids, drugs, and flavorings are just a few of the carbonyl compounds that affect us daily.

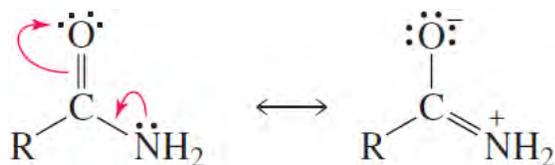
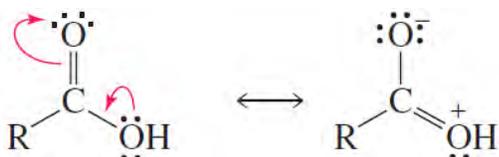
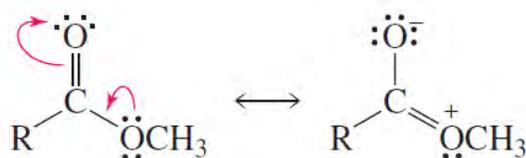
When an alkyl group or to an aryl group is attached to the carbonyl group the species is called an **acyl group**.





The **carbonyl oxygen** is also sp^2 hybridized. One of its sp^2 orbitals forms a σ bond with the carbonyl carbon, and each of the other two sp^2 orbitals contains a lone pair. The remaining p orbital of the carbonyl oxygen overlaps with the remaining p orbital of the carbonyl carbon to form a π bond

For carboxylic acids, esters and amides the unshared electron pairs are delocalized and therefore enable resonance to take place. This can be represented as:



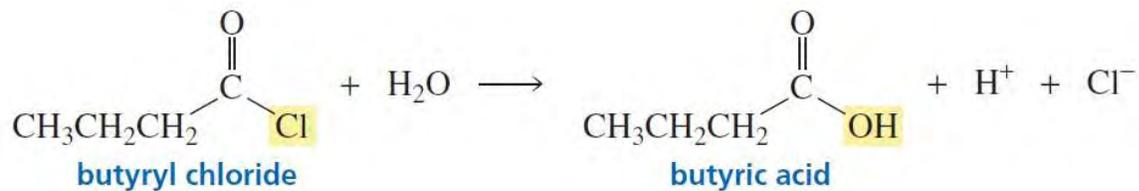
Physical Properties of Carbonyl Compounds

Carbonyl compounds have the following relative boiling points:

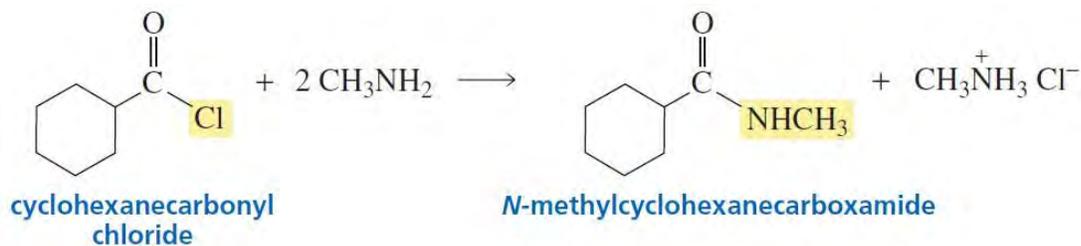
Relative boiling points

amide > carboxylic acid >> ester ~ acyl chloride ~ aldehyde ~ ketone

The boiling points of the **ester**, **acyl chloride**, **ketone**, and **aldehyde** are lower than the boiling point of the **alcohol** with a comparable molecular weight because the molecules of those carbonyl compounds are unable to form **hydrogen bonds** with each other. The boiling points of the carbonyl compounds are higher than the boiling point of the ether because of the polar carbonyl group.

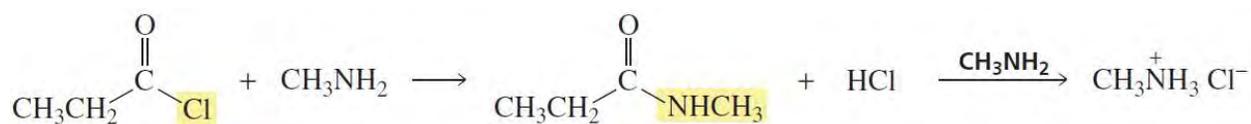
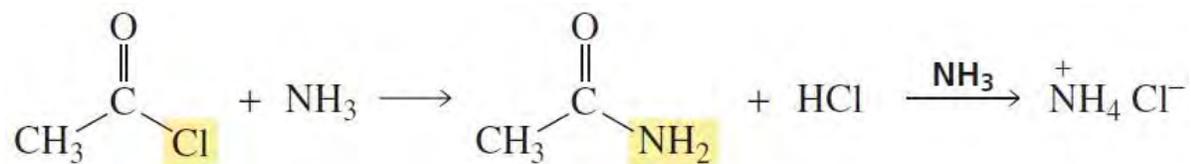


4. with amines to form amides

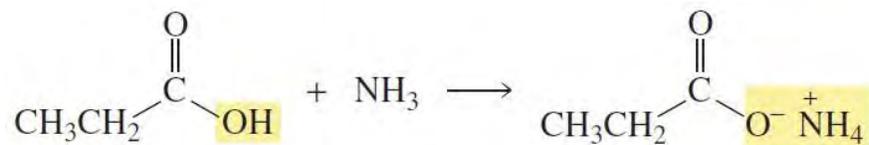
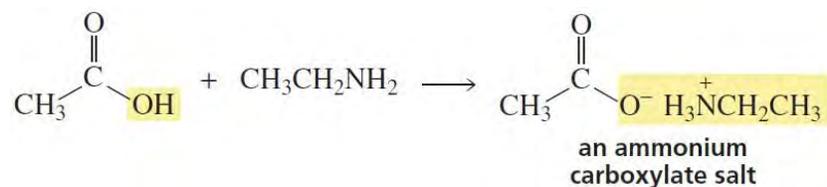


Note that the HCl formed as a byproduct can protonate the unreacted ammonia or unreacted amine. The protonated amines cannot react with the acyl chloride because they are not nucleophiles.

This slows down the reaction.

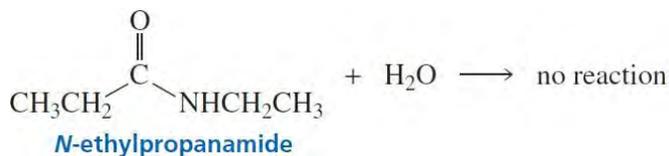
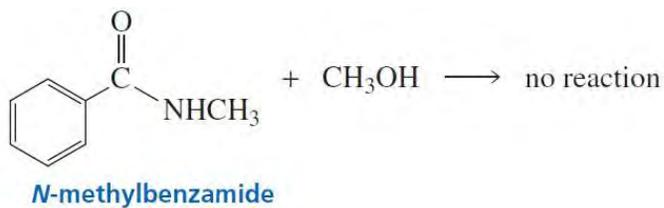
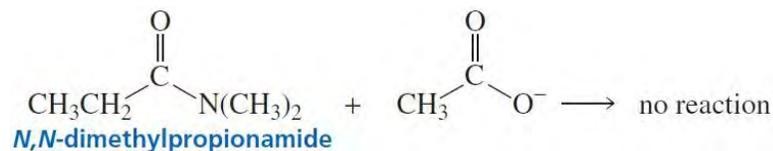
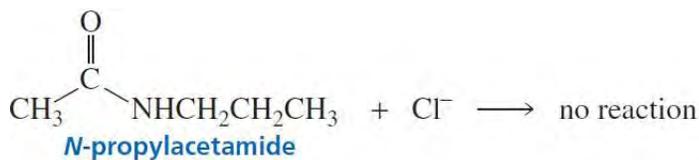


To solve this problem two equivalents ammonia or amine as acyl chloride must be used so that there will be enough amine to react with all the acyl halide.

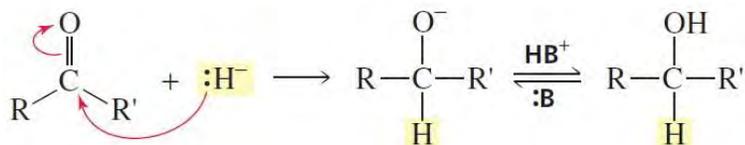


Reactions of Amides

Amides are very unreactive compounds. They do not react with halide ions, carboxylate ions, alcohols, or water because, in each case, the incoming nucleophile is a weaker base than the leaving group of the amide.

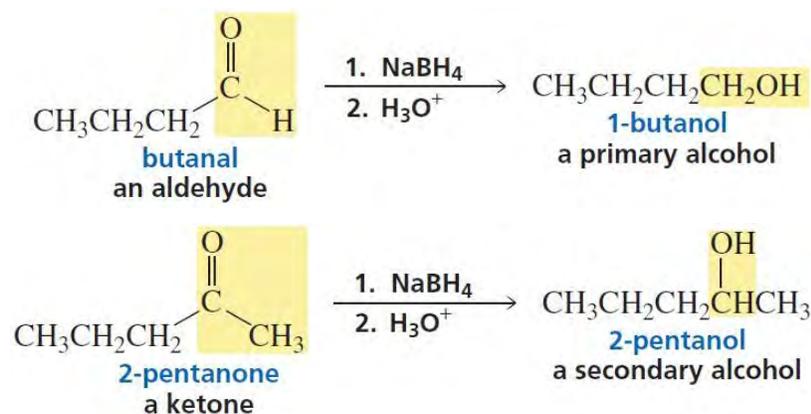


Amides only react with water and alcohols if the reaction mixture is heated in the presence of an acid.



The common source of the hydride ion is sodium borohydride (NaBH_4). Aldehydes are reduced to primary alcohols, and ketones are reduced to secondary alcohols.

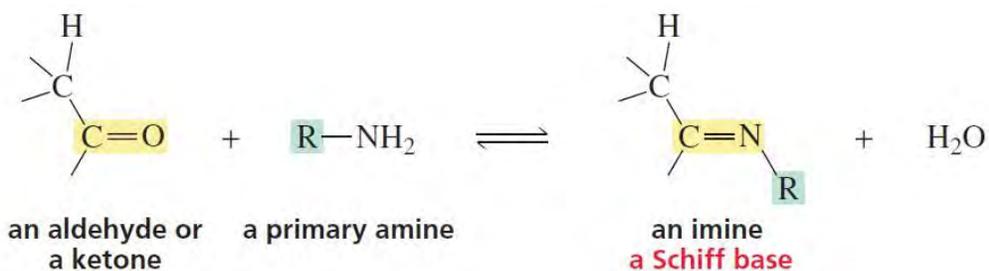
Note that the acid is not added to the reaction mixture until the reaction with the hydride donor is complete.



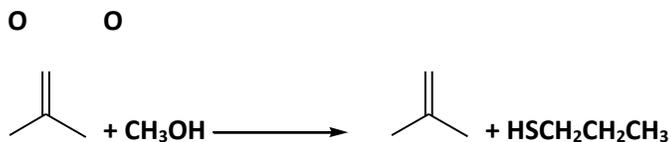
Reactions of Aldehydes and Ketones with Nitrogen Nucleophiles

Aldehydes and ketones react with a **primary amine** (RNH_2) to form an imine. An **imine** is a compound with a carbon–nitrogen double bond.

The imine obtained from the reaction of a carbonyl compound and a primary amine is often called a **Schiff base**.



Examples



Compare with



Methyl benzoate

Ethyl benzoate

The carbon - sulfur bond of a thioester is rather long and delocalization of the sulfur lone-pair electrons into the *p* orbital of the carbonyl group is not as effective as in esters.

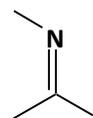
Therefore, Nucleophilic Acyl Substitution reactions of thioesters occur faster than those of simple esters.

IMINE

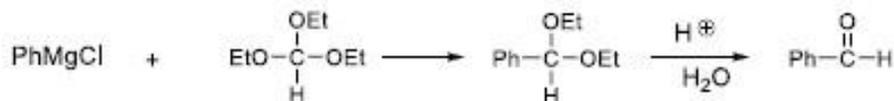
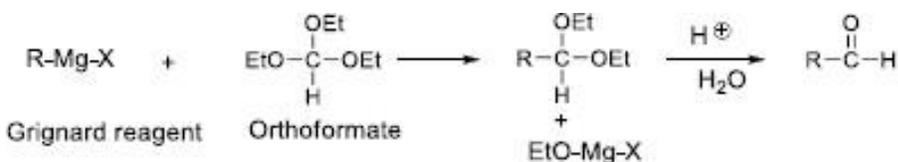
An **imine** is a chemical compound containing a carbon - nitrogen double bond, with the nitrogen attached to a hydrogen atom (H) or an organic group.

The carbon has two additional single bonds.

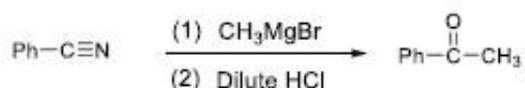
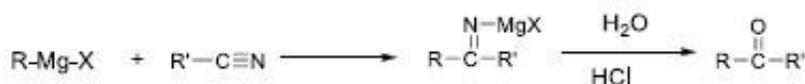
R₁



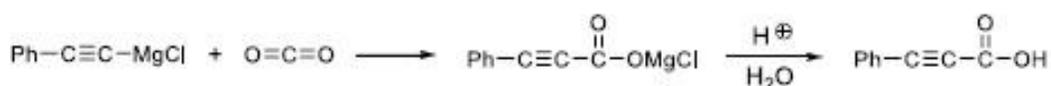
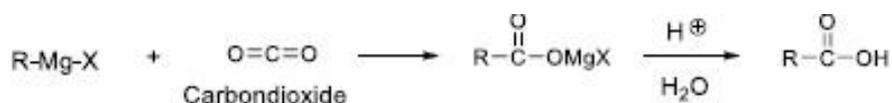
R₂R₃



iv. React with nitriles to iminium salts followed by hydrolysis to provide ketones-
covered earlier



v. React with carbon (IV) oxide followed by acidification to provide carboxylic acids



2. Organo-phosphorus Chemistry- Phosphorus Ylides in Wittig reaction

Phosphorus analogs of amines (NR_3) are known as phosphines (PR_3) which participate as nucleophiles in reactions.

An **ylide**, is defined as a compound with positive and negative charges on adjacent atoms and an overall neutral charge.

There are multiple types of ylides but for the Wittig reaction an **organophosphorus ylide**, also called a **Wittig Reagent**, is be used.

