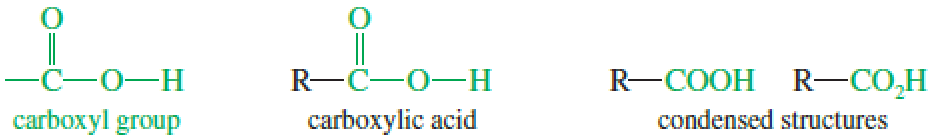
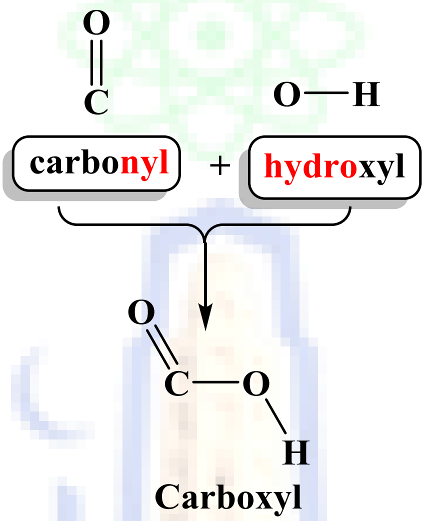
كلية التربية للعلوم الصرفة	الكلية
قسم الكيمياء	القسم
Organic chemistry	المادة باللغة الانجليزية
الكيمياء العضوية	المادة باللغة العربية
المرحلة الثانية	المرحلة الدراسية
د. عمر جمال مهدي العسافي	اسم التدريسي
Carboxylic acids	عنوان المحاضرة باللغة الانجليزية
الحوامض الكاربوكسيلية	عنوان المحاضرة باللغة العربية
الثامنة	رقم المحاضرة
Organic Chemistry 6^{ed} , William H. Brown, Christopher S. Foote, Brent L. Iverson, Eric V. Anslyn, Bruce M. Novak, 2012	المصادر والمراجع
Organic Chemistry 3^{ed} , Janice Gorzynski Smith, 2011	
Organic Chemistry" by Jonathan Clayden, Nick Greeves, and Stuart Warren	

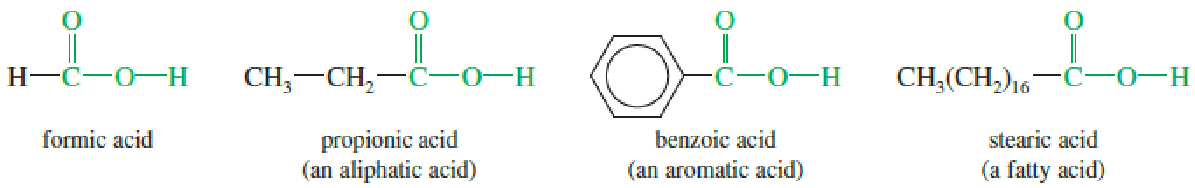
Introduction

The combination of a carbonyl group and a hydroxyl on the same carbon atom is called a carboxyl group. Compounds containing the carboxyl group are distinctly acidic and are called carboxylic acids.



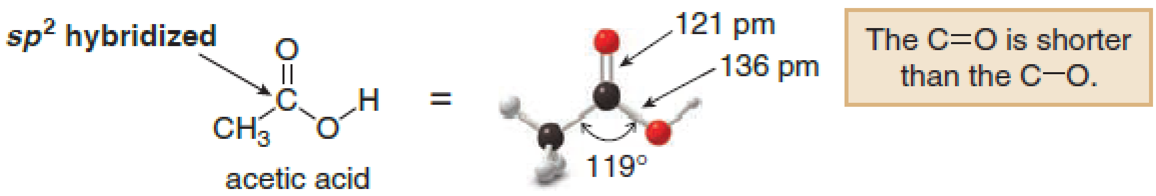


Carboxylic acids are classified according to the substituent bonded to the carboxyl group. An aliphatic acid has an alkyl group bonded to the carboxyl group, and an aromatic acid has an aryl group. The simplest acid is formic acid, with a hydrogen atom bonded to the carboxyl group. Fatty acids are long-chain aliphatic acids derived from the hydrolysis of fats and oils

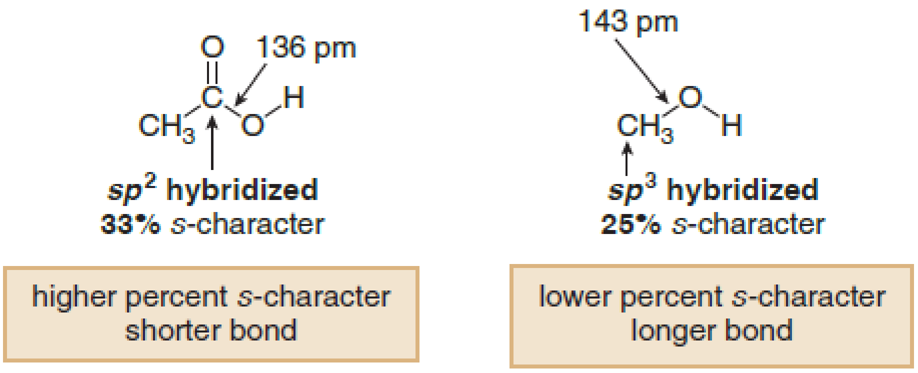


2. Structure and Bonding

The carbon atom of a carboxy group is surrounded by three groups, making it sp2 hybridized and trigonal planar, with bond angles of approximately 120°. The C=O of a carboxylic acid is shorter than its C -O.



The C – O single bond of a carboxylic acid is shorter than the C – O single bond of an alcohol. This can be explained by looking at the hybridization of the respective carbon atoms. In the alcohol, the carbon is sp3 hybridized, whereas in the carboxylic acid the carbon is sp2 hybridized. As a result, the higher percent s-character in the sp2 hybrid orbital shortens the C – O bond in the carboxylic acid.



3. Nomenclature

IUPAC System

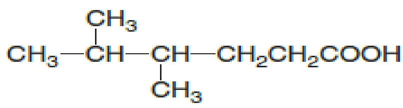
In IUPAC nomenclature, carboxylic acids are identified by a suffix added to the parent name of the longest chain, and two different endings are used depending on whether the carboxy group is bonded to a chain or ring.

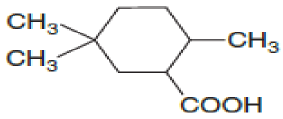
To name a carboxylic acid using the IUPAC system:

[1] If the COOH is bonded to a chain of carbons, find the longest chain containing the COOH group, and change the -e ending of the parent alkane to the suffix -oic acid. If the COOH group is bonded to a ring, name the ring and add the words carboxylic acid.

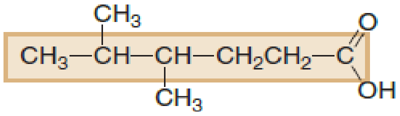
[2] Number the carbon chain or ring to put the COOH group at C1, but omit this number from the name. Apply all of the other usual rules of nomenclature.

Problem Give the IUPAC name of each compound.

a. 

b. 

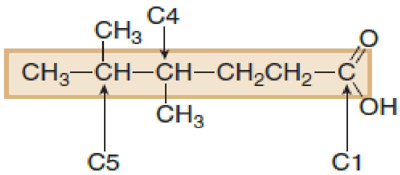
a. [1] Find and name the longest chain containing COOH:



hexane ⟶ **hexan*oic acid***
(6 C's)

The COOH contributes one C to the longest chain.

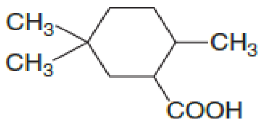
[2] Number and name the substituents:



two methyl substituents on C4 and C5

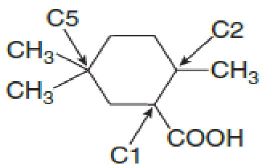
Answer: 4,5-dimethylhexanoic acid

b. [1] Find and name the ring bonded to COOH.



cyclohexane + carboxylic acid
(6 C's)

[2] Number and name the substituents:

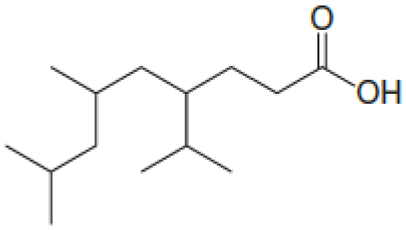


[Number to put COOH at C1 and give the second substituent (CH_3) the lower number (C2).]

Answer: 2,5,5-trimethylcyclohexanecarboxylic acid

Problem Give the IUPAC name for each compound.

a. $CH_3CH_2CH_2C(CH_3)_2CH_2COOH$
b. $CH_3CH(Cl)CH_2CH_2COOH$
c. $(CH_3CH_2)_2CHCH_2CH(CH_2CH_3)COOH$

d. 

Problem Give the structure corresponding to each IUPAC name.

a. 2-bromobutanoic acid

b. 2,3-dimethylpentanoic acid

c. 3,3,4-trimethylheptanoic acid

d. 2-*sec*-butyl-4,4-diethylnonanoic acid

e. 3,4-diethylcyclohexanecarboxylic acid

f. 1-isopropylcyclobutanecarboxylic acid

Common Names

Most simple carboxylic acids have common names that are more widely used than their IUPAC names .A common name is formed by using a common parent name followed by the suffix -ic acid.

Greek letters are used to designate the location of substituents in common names.

• The carbon adjacent to the COOH is called the α carbon.

• The carbon bonded to the α carbon is the a β carbon, followed by the γ (gamma) carbon, the δ (delta) carbon, and so forth down the chain. The last carbon in the chain is sometimes called the Ω (omega) carbon.

The α carbon in the common system is numbered C2 in the IUPAC system.

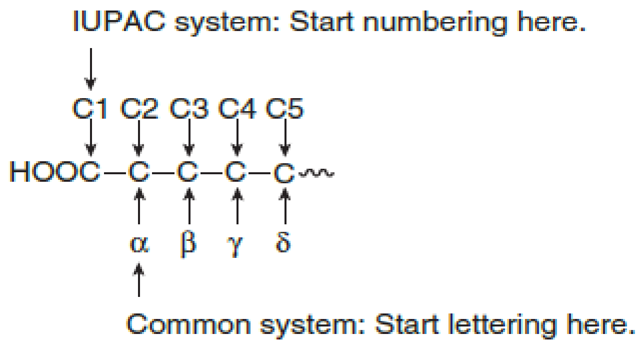
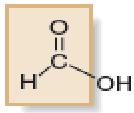
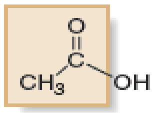
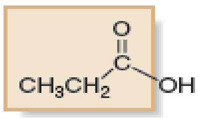
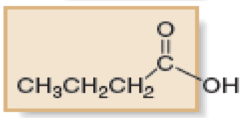
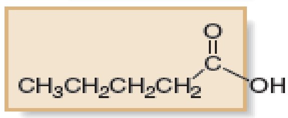
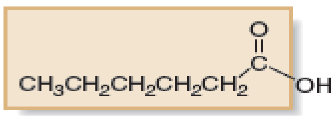
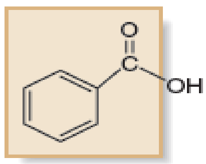


Table Common Names for Some Simple Carboxylic Acids

Number of C atoms	Structure	Parent name	Common name
1		**form-**	formic acid
2		**acet-**	acetic acid
3		**propion-**	propionic acid
4		**butyr-**	butyric acid
5		**valer-**	valeric acid
6		**capro-**	caproic acid
		**benzo-**	benzoic acid

Problem Draw the structure corresponding to each common name:

a. α-methoxyvaleric acid
b. β-phenylpropionic acid
c. α,β-dimethylcaproic acid
d. α-chloro-β-methylbutyric acid

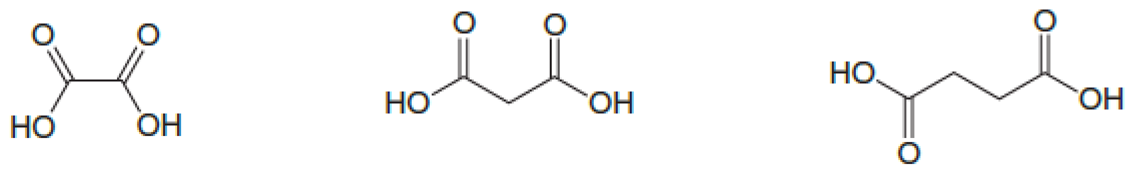
Problem Give an IUPAC and common name for each of the following naturally occurring carboxylic acids:

(a) $CH_3CH(OH)CO_2H$ (lactic acid)

(b) $HOCH_2CH_2C(OH)(CH_3)CH_2CO_2H$ (mevalonic acid).

Nomenclature of Dicarboxylic Acids

Many compounds containing two carboxy groups are also known. In the IUPAC system, diacids are named by adding the suffix -dioic acid to the name of the parent alkane. The three simplest diacids are most often identified by their common names, as shown.



oxalic acid (ethanedioic acid) **malonic acid** (propanedioic acid) **succinic acid** (butanedioic acid)

Names of Dicarboxylic Acids

IUPAC Name	Common Name	Formula
ethanedioic	oxalic	HOOC—COOH
propanedioic	malonic	$HOOCCH_2COOH$
butanedioic	succinic	$HOOC(CH_2)_2COOH$
pentanedioic	glutaric	$HOOC(CH_2)_3COOH$
hexanedioic	adipic	$HOOC(CH_2)_4COOH$
heptanedioic	pimelic	$HOOC(CH_2)_5COOH$
cis-but-2-enedioic	maleic	*cis*-HOOCCH═CHCOOH
trans-but-2-enedioic	fumaric	*trans*-HOOCCH═CHCOOH
benzene-1,2-dicarboxylic	phthalic	1,2-$C_6H_4(COOH)_2$
benzene-1,3-dicarboxylic	isophthalic	1,3-$C_6H_4(COOH)_2$
benzene-1,4-dicarboxylic	terephthalic	1,4-$C_6H_4(COOH)_2$

Metal salts of carboxylate anions are formed from carboxylic acids in many reactions. To name the metal salt of a carboxylate anion, change the *-ic acid* ending of the carboxylic acid to the suffix -ate and put three parts together:

name of the metal cation + parent + suffix

parent: common or IUPAC

suffix: ***-ate***

Problem Give the IUPAC name for each metal salt of a carboxylate anion:

(a) $C_6H_5CO_2^- \ Li^+$

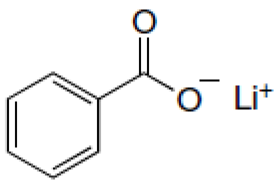
(b) $HCO_2^- \ Na^+$

(c) $(CH_3)_2CHCO_2^- \ K^+$

(d) $(CH_3CH_2)_2CHCH_2CH(Br)CH_2CH_2CO_2^- \ Na^+$

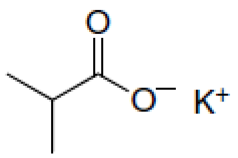
Solution:-

a.



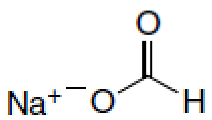
lithium benzoate

c.



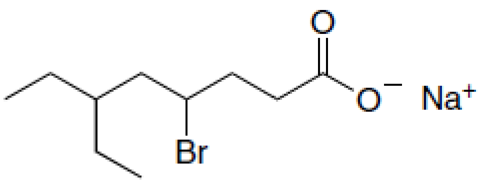
potassium 2-methylpropanoate

b.

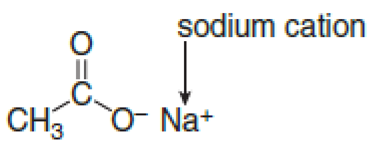


sodium formate
or
sodium methanoate

d.

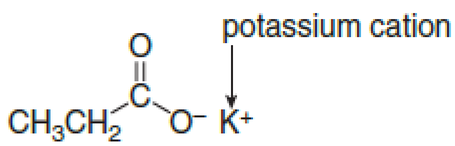


sodium 4-bromo-6-ethyl-octanoate



parent + suffix
acet- -ate

sodium acetate



parent + suffix
propano- -ate

potassium propanoate

Problem: Give IUPAC names for each of these compounds:

[$(CH_3CH_2CH_2)_2CHCO_2H$] and its sodium salt.

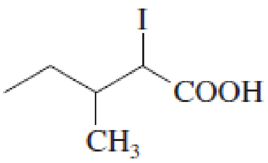
PROBLEM 1

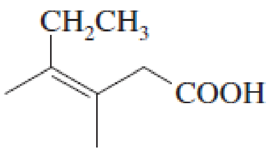
Draw the structures of the following carboxylic acids.

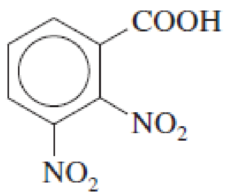
(a) α-methylbutyric acid
(b) 2-bromobutanoic acid
(c) 4-aminopentanoic acid
(d) *cis*-4-phenylbut-2-enoic acid
(e) *trans*-2-methylcyclohexanecarboxylic acid
(f) 2,3-dimethylfumaric acid
(g) *m*-chlorobenzoic acid
(h) 3-methylphthalic acid
(i) β-aminoadipic acid
(j) 3-chloroheptanedioic acid
(k) 4-oxoheptanoic acid
(l) phenylacetic acid

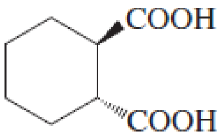
PROBLEM 2

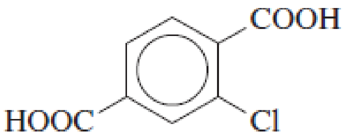
Name the following carboxylic acids (when possible, give both a common name and a systematic name).

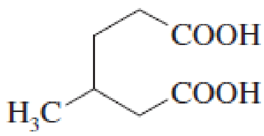
(a)


(b)


(c)


(d)


(e)


(f)


4. Physical Properties

Carboxylic acids exhibit dipole–dipole interactions because they have polar C – O and O – H bonds. They also exhibit intermolecular hydrogen bonding because they possess a hydrogen atom bonded to an electronegative oxygen atom. Carboxylic acids often exist as dimers, held together by two intermolecular hydrogen bonds between the carbonyl oxygen atom of one molecule and the OH hydrogen atom of another molecule . Carboxylic acids are the most polar organic compounds we have studied so far. How these intermolecular forces affect the physical properties of carboxylic acids is summarized in Table.

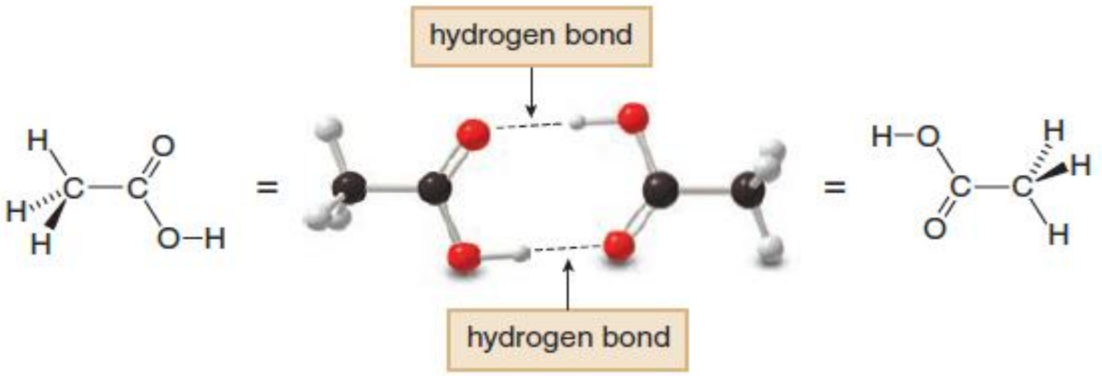


Table Physical Properties of Carboxylic Acids

Property	Observation
Boiling point and melting point	• Carboxylic acids have higher boiling points and melting points than other compounds of comparable molecular weight. $CH_3CH_2CH_2CH_3$ (VDW; MW = 58; bp 0 °C); CH_3CH_2CHO (VDW, DD; MW = 58; bp 48 °C); $CH_3CH_2CH_2OH$ (VDW, DD, HB; MW = 60; bp 97 °C); CH_3COOH (VDW, DD, two HB; MW = 60; bp 118 °C) **Increasing strength of intermolecular forces** **Increasing boiling point**
Solubility	• Carboxylic acids are soluble in organic solvents regardless of size. • Carboxylic acids having ≤ 5 C's are water soluble because they can hydrogen bond with H_2O • Carboxylic acids having > 5 C's are water insoluble because the nonpolar alkyl portion is too large to dissolve in the polar H_2O solvent. These "fatty" acids dissolve in a nonpolar fat-like environment but do not dissolve in water.

Key: VDW = van der Waals, DD = dipole–dipole, HB = hydrogen bonding, MW = molecular weight

5. Synthesis of Carboxylic Acids

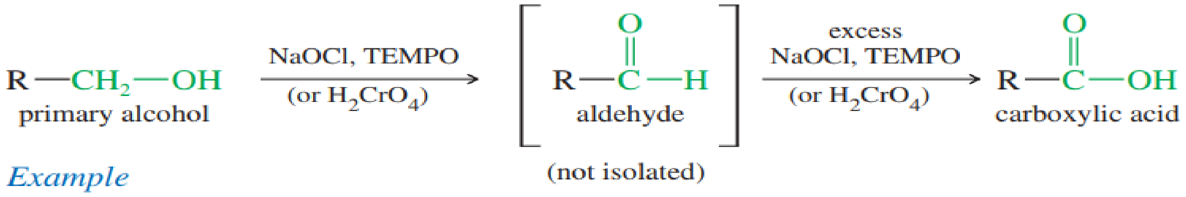
We have already encountered three methods for preparing carboxylic acids:

(1) oxidation of alcohols and aldehydes

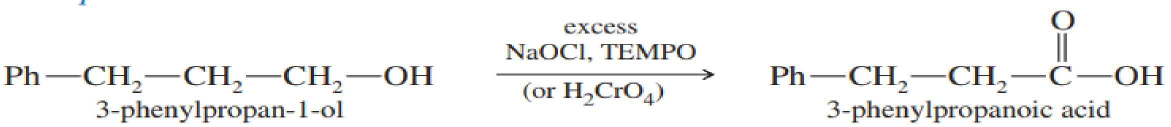
(2) oxidative cleavage of alkenes and alkynes

(3) severe side-chain oxidation of alkylbenzenes.

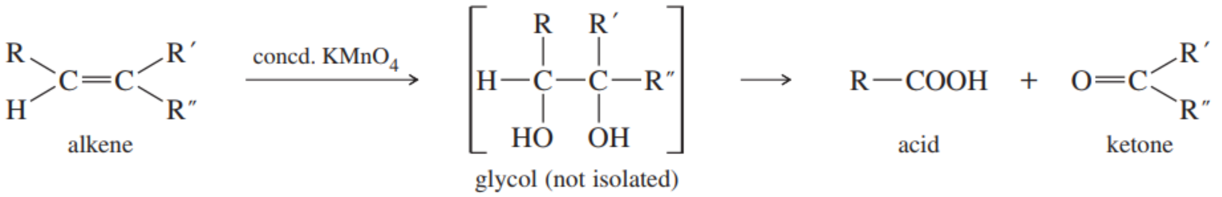
1. Primary alcohols and aldehydes are commonly oxidized to acids by sodium hypochlorite (bleach, NaOCl), often used with TEMPO as a catalyst, or by chromic acid, H2CrO4



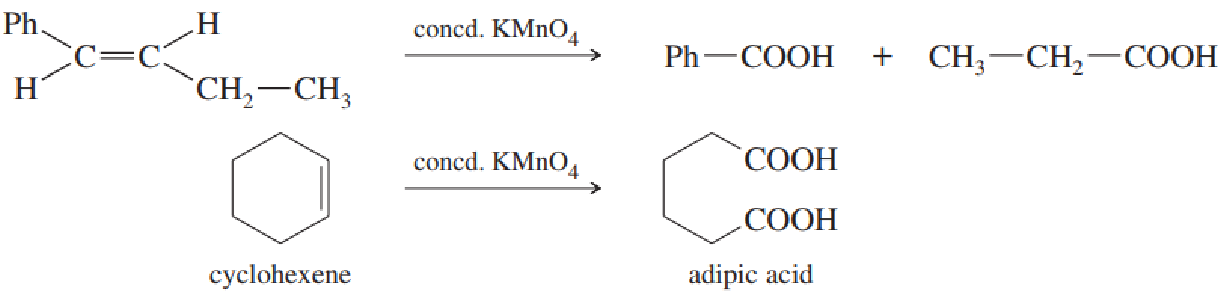
Example



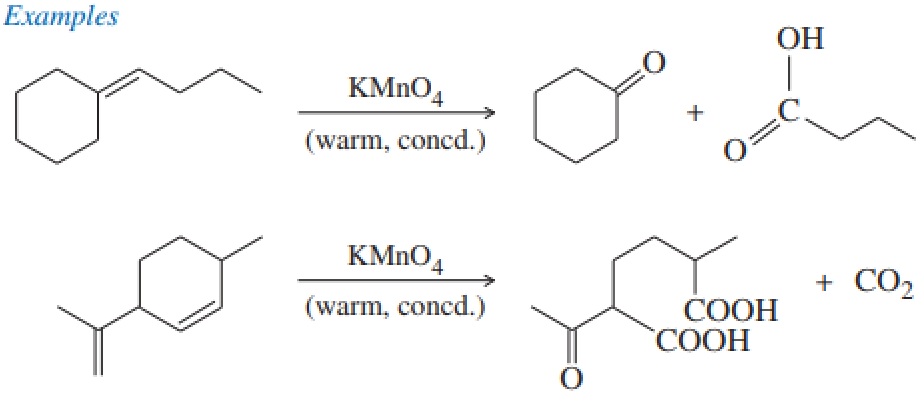
2.Cold, dilute potassium permanganate reacts with alkenes to give glycols. Warm, concentrated permanganate solutions oxidize the glycols further, cleaving the central carbon–carbon bond. Depending on the substitution of the original double bond, ketones or acids may result .



Examples

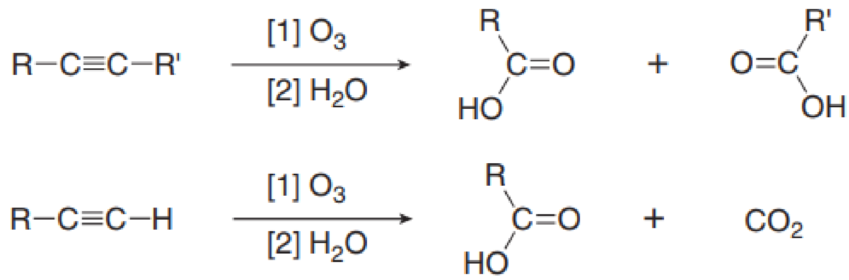


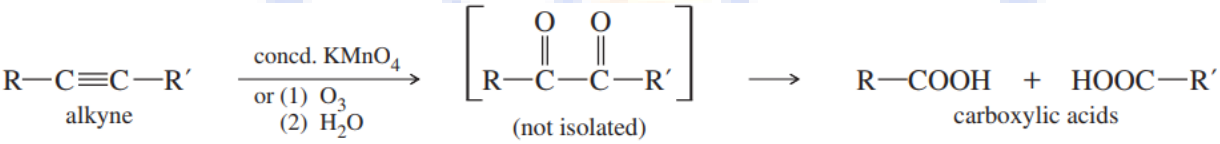
Examples



With alkynes, either ozonolysis or a vigorous permanganate oxidation cleaves the triple bond to give carboxylic acids

General reactions

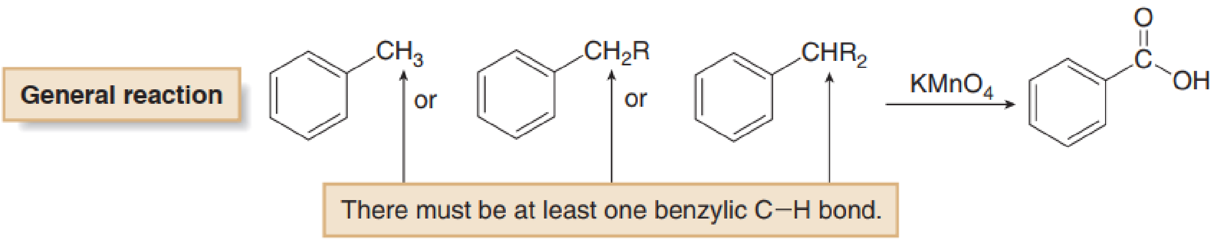


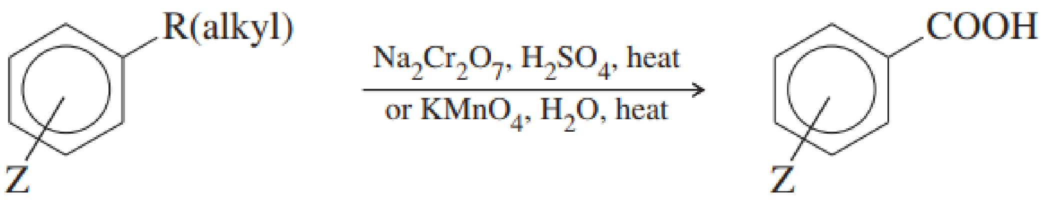


Example

$$CH_3CH_2CH_2—C\equiv C—Ph \xrightarrow[(2)\ H_2O]{(1)\ O_3} CH_3CH_2CH_2—COOH + Ph—COOH$$

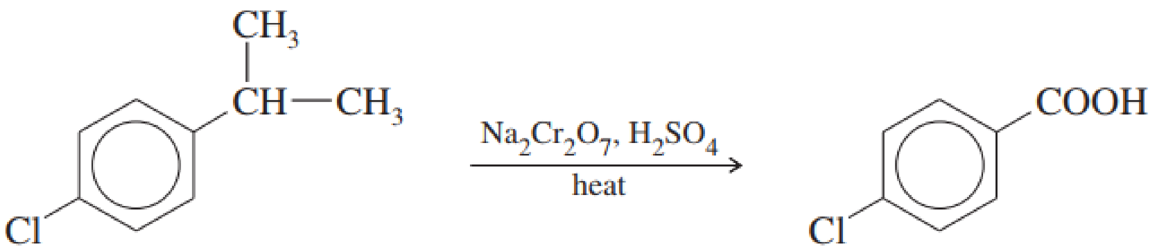
3.Side chains of alkylbenzenes are oxidized to benzoic acid derivatives by treatment with hot potassium permanganate or hot chromic acid. Because this oxidation requires severe conditions, it is useful only for making benzoic acid derivatives with no oxidizable functional groups. Oxidation-resistant functional groups such as ¬ Cl, ¬ NO2, ¬ SO3H, and ¬ COOH may be present.





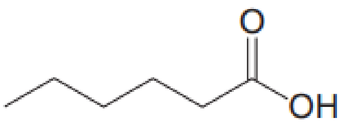
an alkylbenzene (Z must be oxidation-resistant) — a benzoic acid

Example

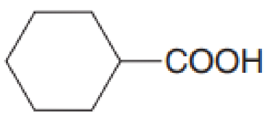


p-chloroisopropylbenzene — *p*-chlorobenzoic acid

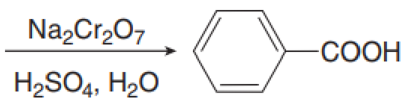
Problem What alcohol can be oxidized to each carboxylic acid?

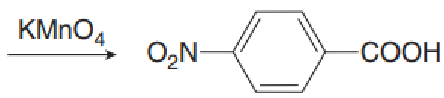
a. 

b. $(CH_3)_2CHCOOH$

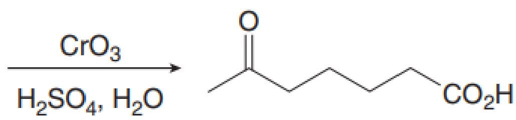
c. 

Problem Identify **A–D** in the following reactions.

a. **A** 

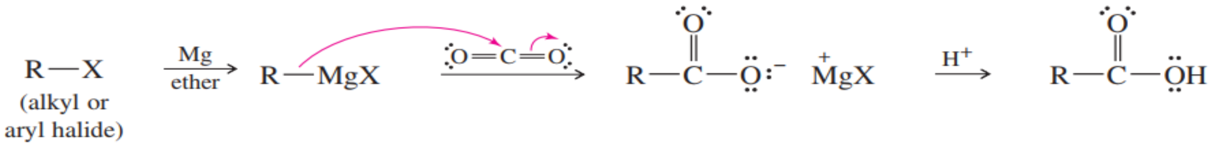
c. **C** 

b. **B** $\xrightarrow[\text{[2] } H_2O]{\text{[1] } O_3}$ CH_3COOH (2 equiv)

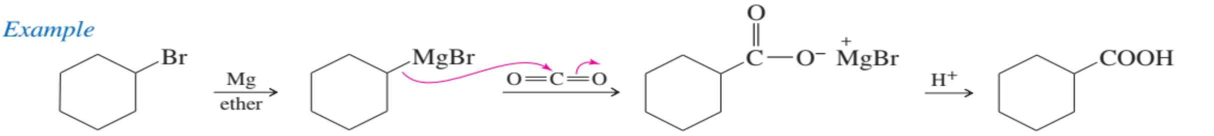
d. **D** 

Carboxylation of Grignard Reagents

Grignard reagents add to carbon dioxide to form magnesium salts of carboxylic acids. Addition of dilute acid protonates these magnesium salts to give carboxylic acids. This method is useful because it converts a halide functional group to a carboxylic acid functional group with an additional carbon atom.



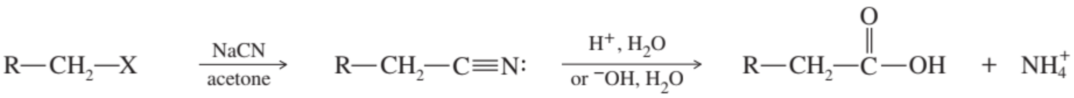
Example



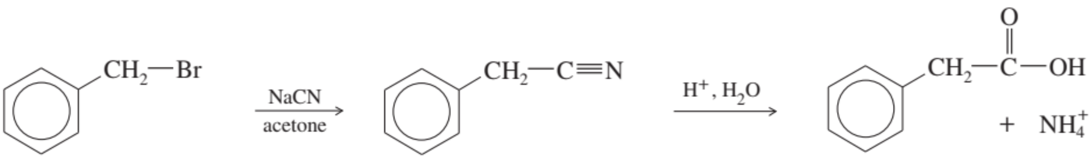
Formation and Hydrolysis of Nitriles

Another way to convert an alkyl halide (or tosylate) to a carboxylic acid with an additional carbon atom is to displace the halide with sodium cyanide. The product is a nitrile with one additional carbon atom. Acidic or basic hydrolysis of the nitrile gives a carboxylic acid.

This method is limited to halides and tosylates that are good S_N2 electrophiles: usually primary and unhindered.



Example



PROBLEM

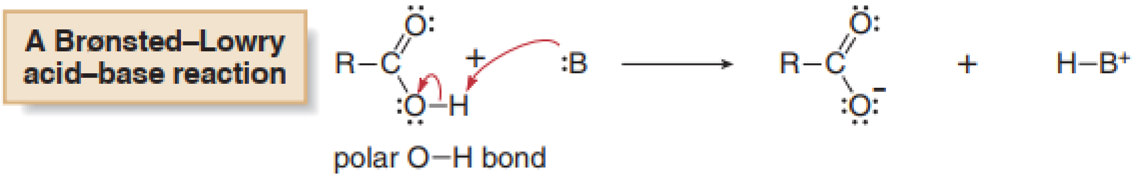
Show how you would synthesize the following carboxylic acids, using the indicated starting materials.

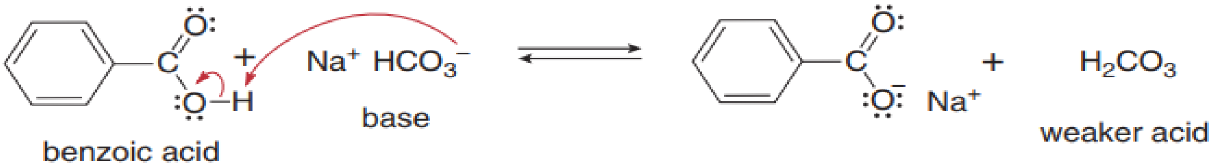
(a) oct-4-yne → butanoic acid
(b) *trans*-cyclodecene → decanedioic acid
(c) bromobenzene → phenylacetic acid
(d) butan-2-ol → 2-methylbutanoic acid
(e) *p*-xylene → terephthalic acid
(f) allyl iodide → but-3-enoic acid

Reactions of Carboxylic Acids

The polar C – O and O – H bonds, nonbonded electron pairs on oxygen, and the π bond give a carboxylic acid many reactive sites, complicating its chemistry somewhat. By far, the most important reactive feature of a carboxylic acid is its polar O – H bond, which is readily cleaved with base.

Carboxylic acids react as Brønsted–Lowry acids—that is, as proton donors.





Because the pKa values of many carboxylic acids are ~5, bases that have conjugate acids with pKa values higher than 5 are strong enough to deprotonate them. Thus, acetic acid (pKa = 4.8) and benzoic acid (pKa = 4.2) can be deprotonated with NaOH and NaHCO3, as shown in the following equations.

Examples

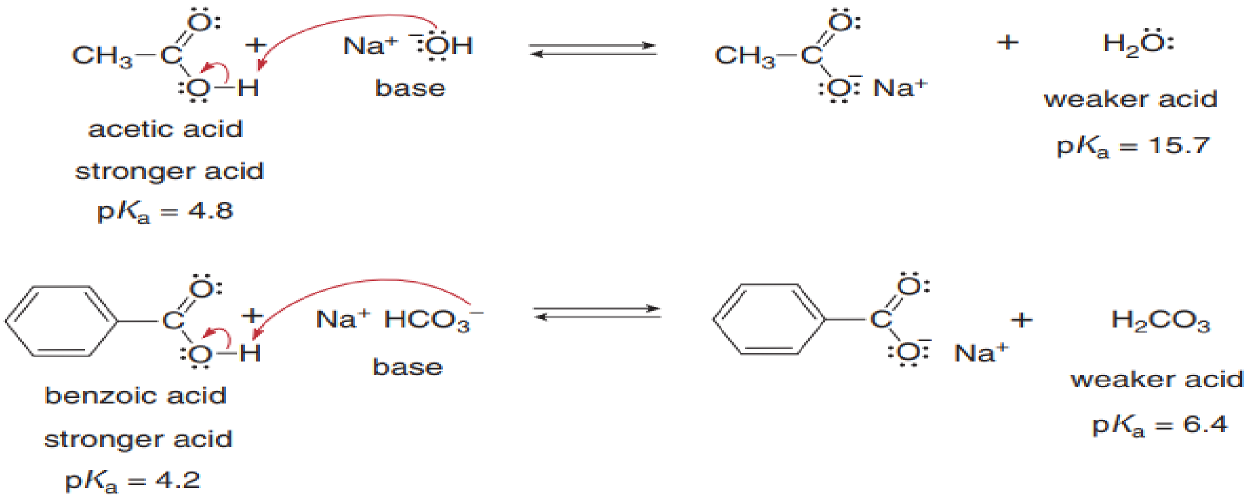


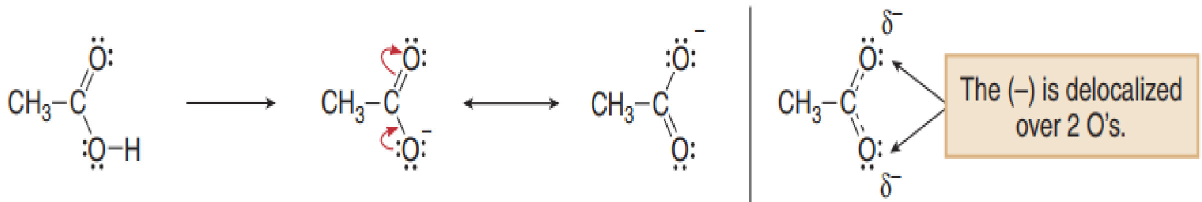
Table below lists common bases that can be used to deprotonate carboxylic acids. It is noteworthy that even a weak base like NaHCO3 is strong enough to remove a proton from RCOOH.

Table Common Bases Used to Deprotonate Carboxylic Acids

Increasing basicity ↓

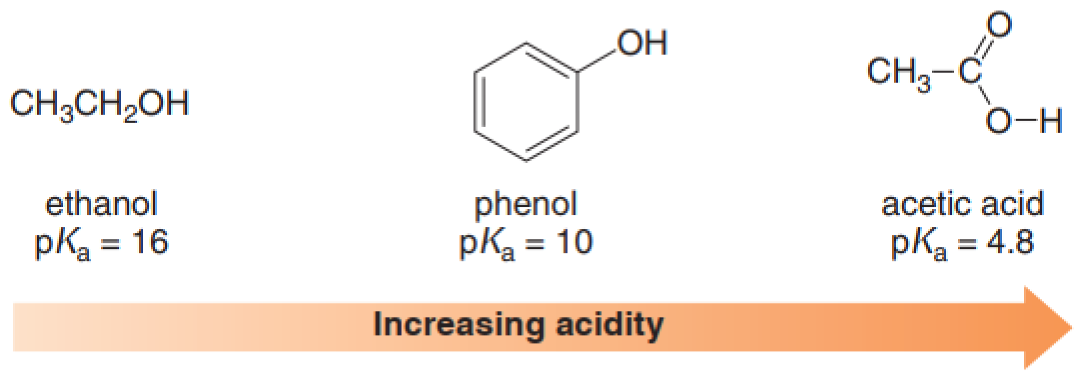
Base	Conjugate acid (pK_a)
$Na^+\ HCO_3^-$	H_2CO_3 (6.4)
NH_3	NH_4^+ (9.4)
Na_2CO_3	HCO_3^- (10.2)
$Na^+\ ^-OCH_3$	CH_3OH (15.5)
$Na^+\ ^-OH$	H_2O (15.7)
$Na^+\ ^-OCH_2CH_3$	CH_3CH_2OH (16)
$Na^+\ H^-$	H_2 (35)

Why are carboxylic acids such strong organic acids? Remember that a strong acid has a weak, stabilized conjugate base. Deprotonation of a carboxylic acid forms a resonance-stabilized conjugate base—a carboxylate anion. For example, two equivalent resonance structures can be drawn for acetate (the conjugate base of acetic acid), both of which place a negative charge on an electronegative O atom. In the resonance hybrid, therefore, the negative charge is delocalized over two oxygen atoms.

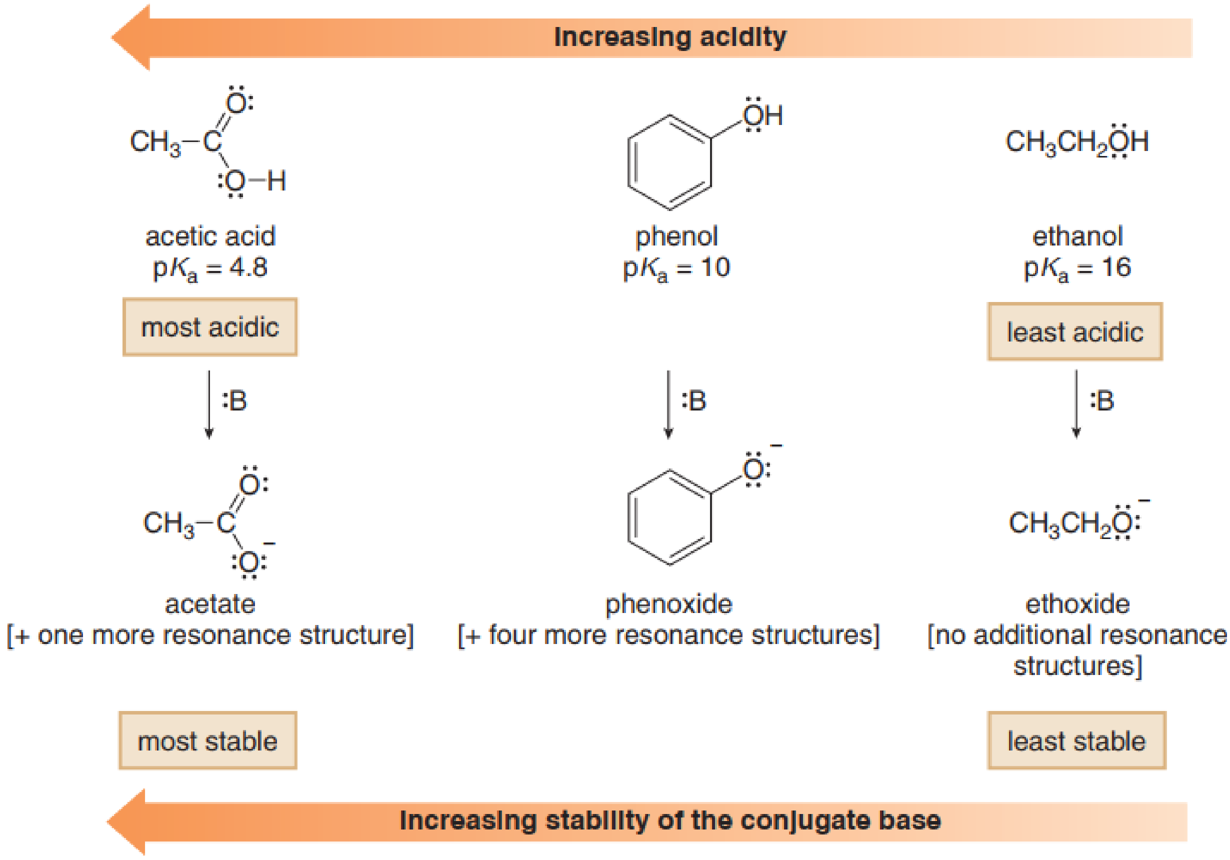


acetic acid — two resonance structures for acetate, the conjugate base — hybrid

Resonance stabilization accounts for why carboxylic acids are more acidic than other compounds with O – H bonds—namely, alcohols and phenols.



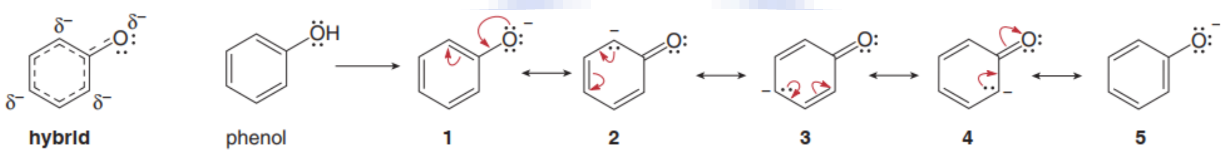
The relationship between acidity and conjugate base stability for acetic acid, phenol, and ethanol



Acetate is the most stable conjugate base because it has two equivalent resonance structures, both of which place a negative charge on an O atom.

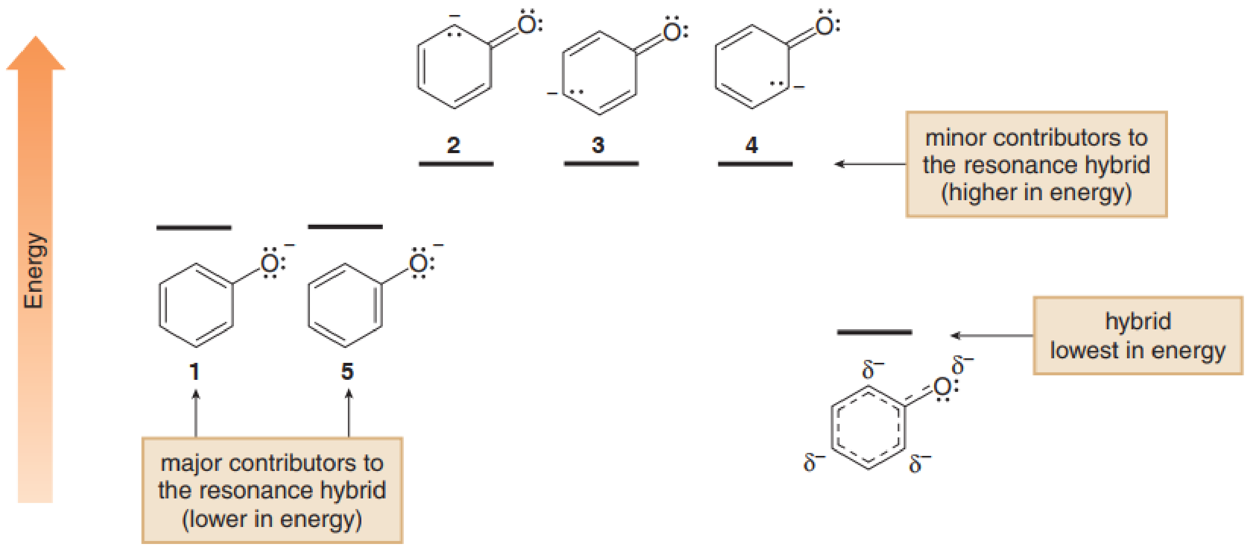
• Phenoxide has only one O atom to accept the negative charge. The two resonance structures that contain an intact aromatic ring and place a negative charge on an O atom are major contributors to the hybrid. Resonance stabilizes phenoxide but not as much as resonance stabilizes acetate.

• Ethoxide is the least stable conjugate base because it has no additional resonance.



Five resonance structures delocalize the negative charge over four atoms.

Phenoxide is more stable than ethoxide, but less stable than acetate, because acetate has two electronegative oxygen atoms upon which to delocalize the negative charge, whereas phenoxide has only one. Additionally, phenoxide resonance structures 2–4 have the negative charge on a carbon, a less electronegative element than oxygen. As a result, structures 2–4 are less stable than structures 1 and 5, which have the negative charge on oxygen.



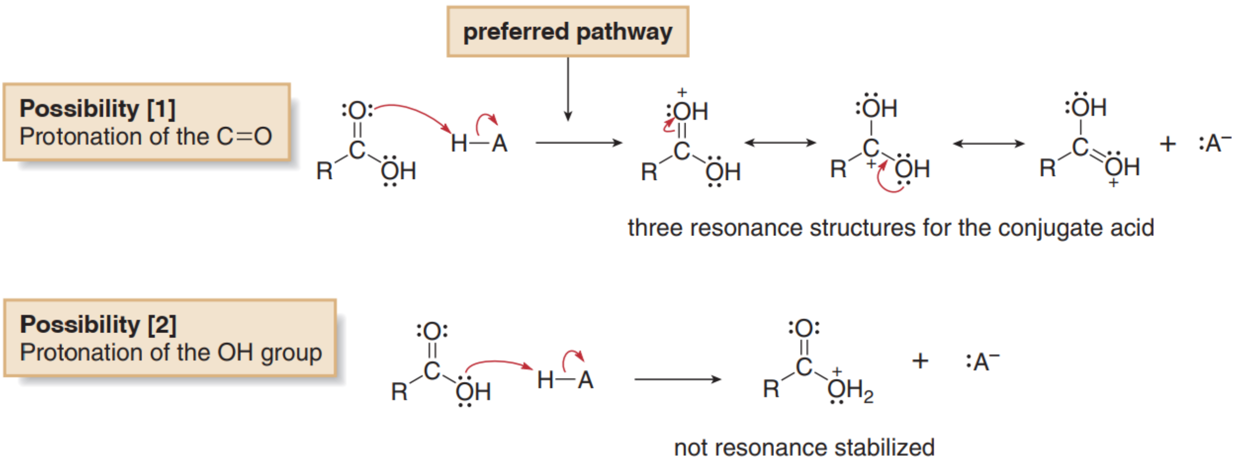
Moreover, resonance structures 1 and 5 have intact aromatic rings, whereas structures 2–4 do not. This, too, makes structures 2–4 less stable than 1 and 5. Figure above summarizes this information about phenoxide by displaying the approximate relative energies of its five resonance structures and its hybrid.

As a result, resonance stabilization of the conjugate base is important in determining acidity, but the absolute number of resonance structures alone is not what's important. We must evaluate their relative contributions to predict the relative stability of the conjugate bases.

• Because of their O – H bond, RCOOH, ROH, and C6H5OH are more acidic than most organic hydrocarbons.

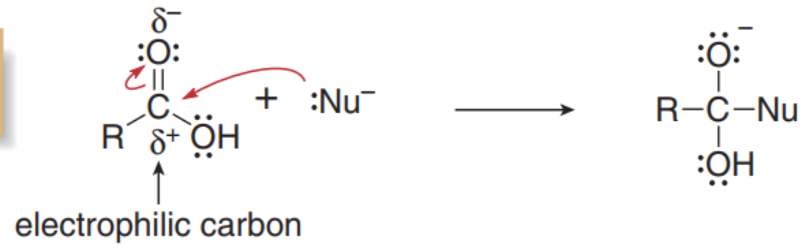
• A carboxylic acid is a stronger acid than an alcohol or phenol because its conjugate base is most effectively resonance stabilized.

The nonbonded electron pairs on oxygen create electron-rich sites that can be protonated by strong acids (H – A). Protonation occurs at the carbonyl oxygen because the resulting conjugate acid is resonance stabilized (Possibility [1]). The product of protonation of the OH group (Possibility [2]) cannot be resonance stabilized. As a result, carboxylic acids are weakly basic—they react with strong acids by protonation of the carbonyl oxygen.



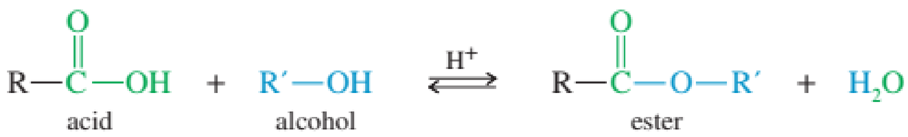
Finally, the polar C – O bonds make the carboxy carbon electrophilic, so carboxylic acids react with nucleophiles. Nucleophilic attack occurs at an sp2 hybridized carbon atom, so it results in the cleavage of the π bond, as well.

Nucleophilic attack at the carboxy carbon

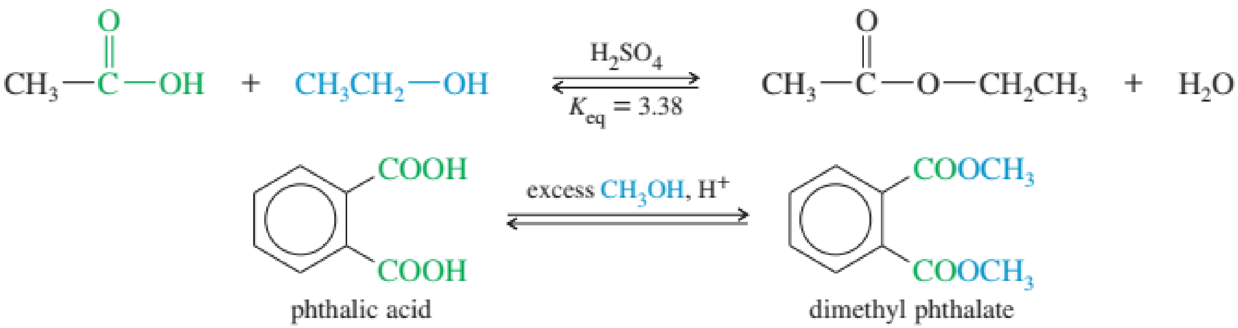


Condensation of Acids with Alcohols:

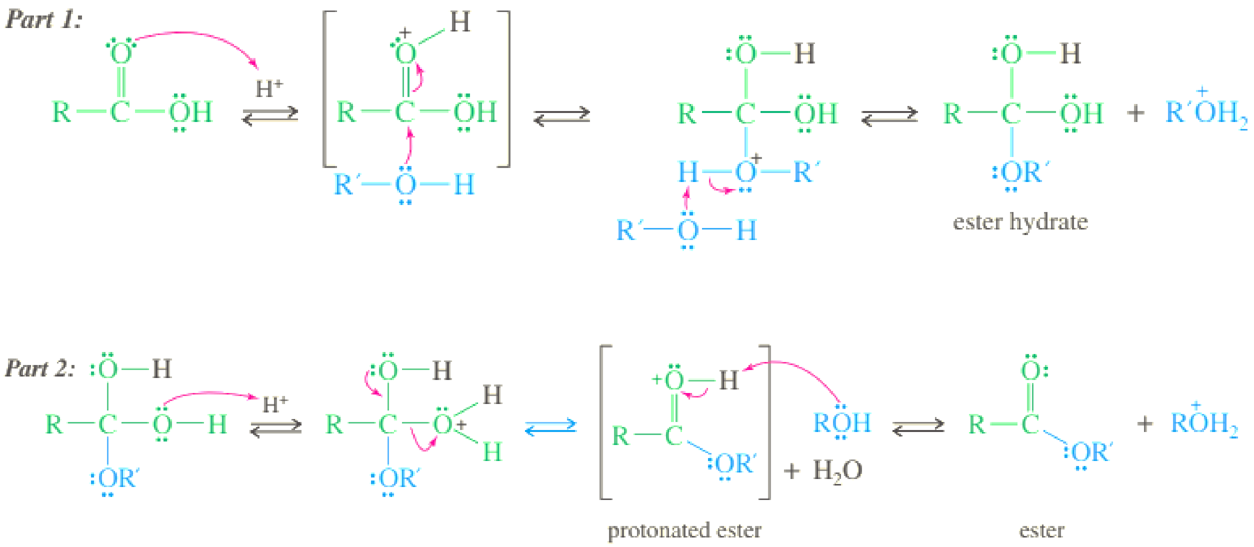
The Fischer Esterification The Fischer esterification converts carboxylic acids and alcohols directly to esters by an acid-catalyzed nucleophilic acyl substitution. The net reaction is replacement of the acid ¬ OH group by the ¬ OR group of the alcohol.



Examples

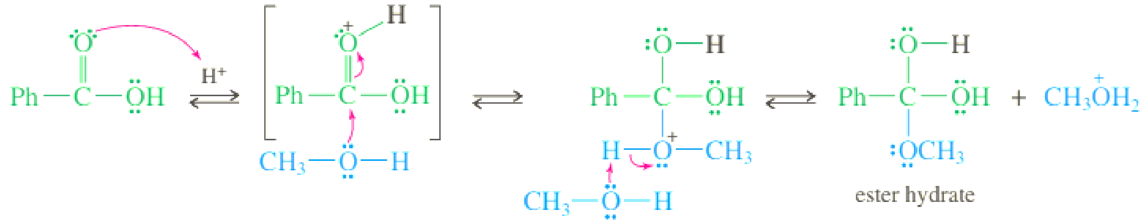


MECHANISM Fischer Esterification

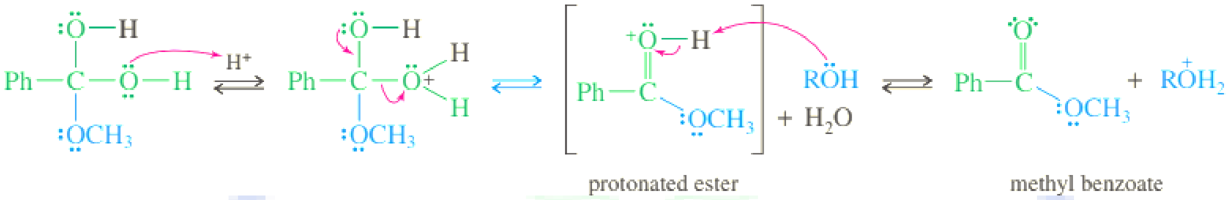


EXAMPLE: Acid-catalyzed formation of methyl benzoate from methanol and benzoic acid.

Part 1: *Acid-catalyzed addition of methanol to the carbonyl group.*

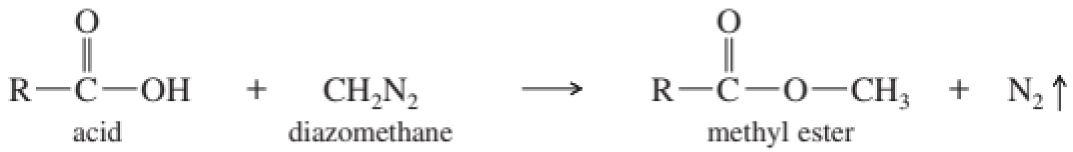


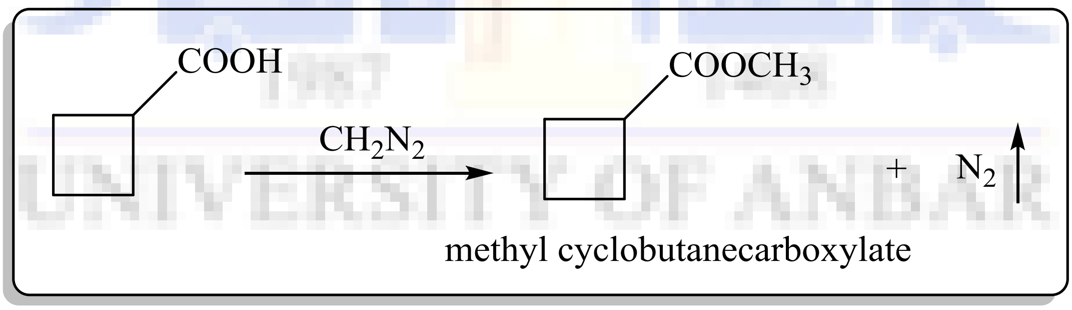
Part 2: *Acid-catalyzed dehydration.*



Esterification Using Diazomethane

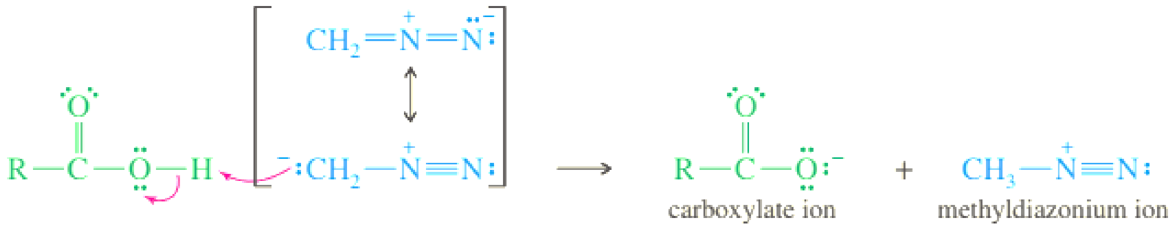
Carboxylic acids are converted to their methyl esters very simply by adding an ether solution of diazomethane. The only by-product is nitrogen gas, and any excess diazomethane also evaporates. Purification of the ester usually involves only evaporation of the solvent. Yields are nearly quantitative in most cases



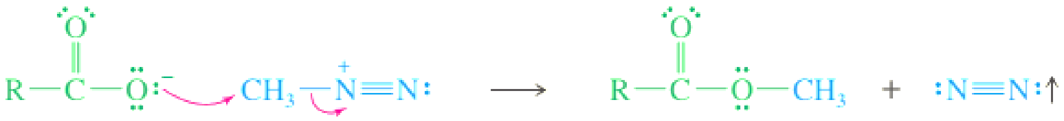


MECHANISM Esterification Using Diazomethane

Step 1: Proton transfer, forming a carboxylate ion and a methyldiazonium ion.

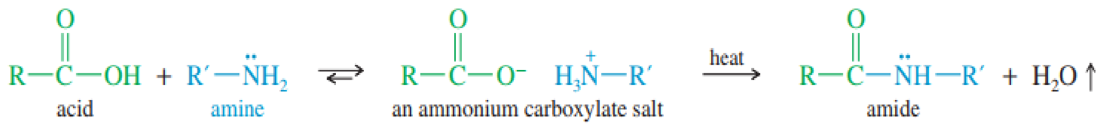


Step 2: Nucleophilic attack on the methyl group displaces nitrogen.

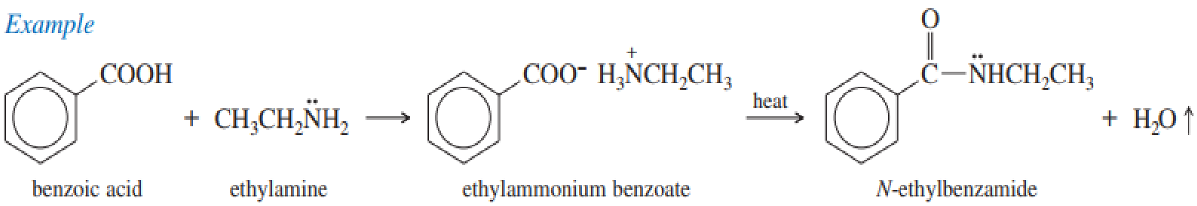


Condensation of Acids with Amines: Direct Synthesis of Amides

Amides can be synthesized directly from carboxylic acids, using heat to drive off water and force the reaction to completion. The initial acid–base reaction of a carboxylic acid with an amine gives an ammonium carboxylate salt. The carboxylate ion is a poor electrophile, and the ammonium ion is not nucleophilic, so the reaction stops at this point. Heating this salt to well above 100 °C drives off steam and forms an amide. This direct synthesis is an important industrial process, and it often works well in the laboratory.

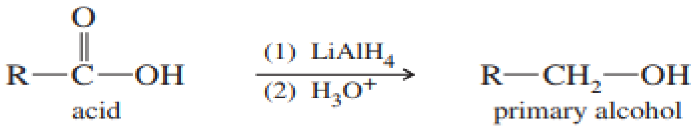


Example

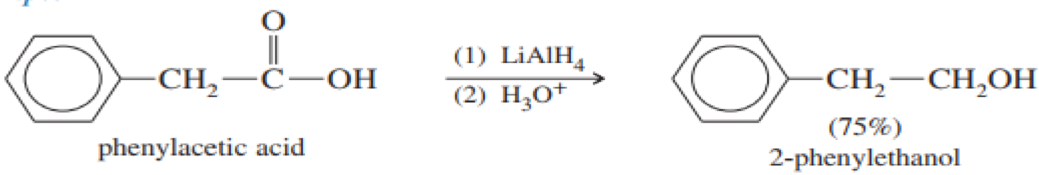


Reduction of Carboxylic Acids

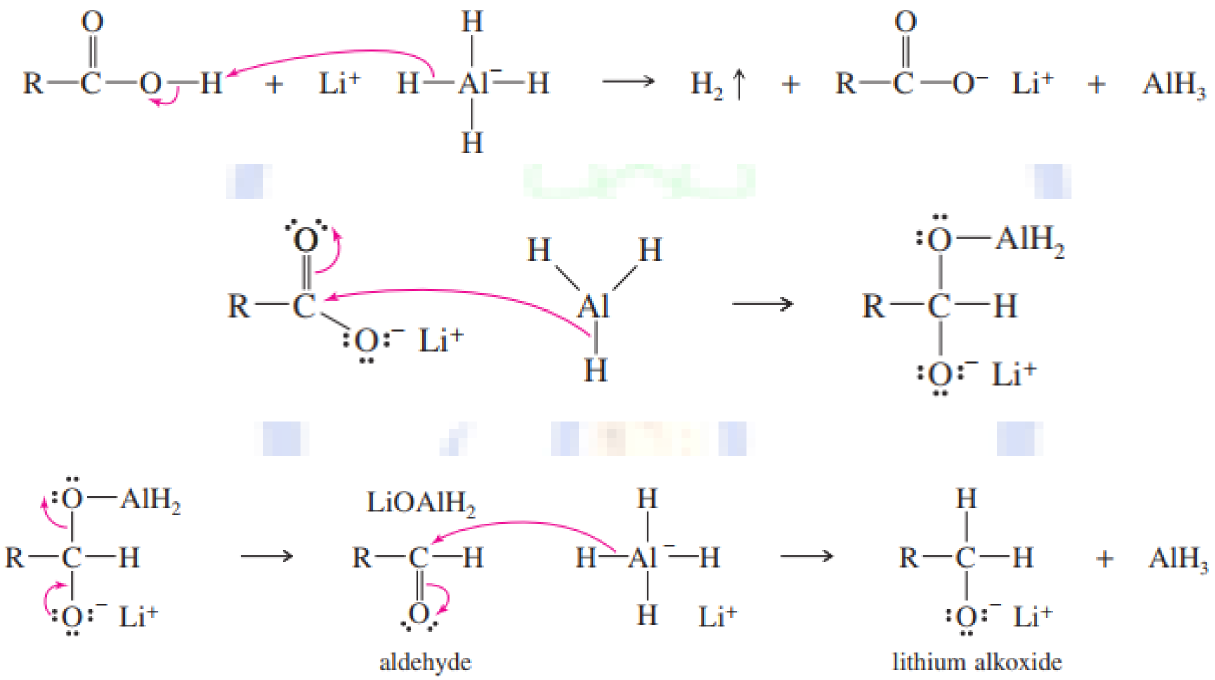
Carboxylic acids are reduced to 1° alcohols with LiAlH4. LiAlH4 is too strong a reducing agent to stop the reaction at the aldehyde stage, but milder reagents are not strong enough to initiate the reaction in the first place, so this is the only useful reduction reaction of carboxylic acids



Example



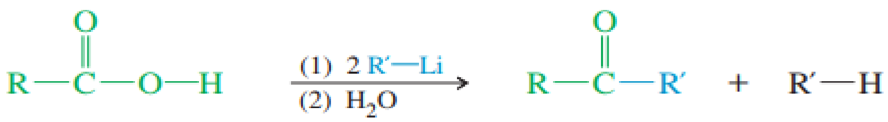
MECHANISM of Reduction



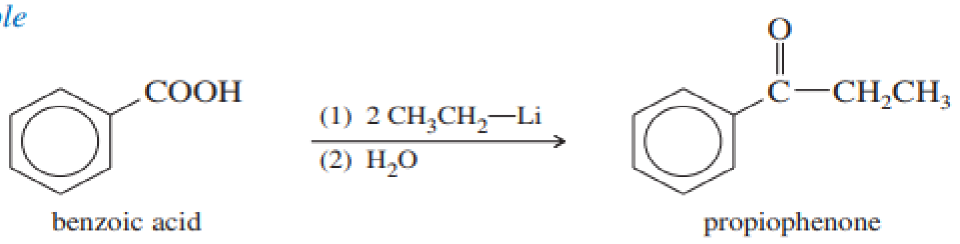
$$R-CH_2-O^- \; Li^+ + H_2O \longrightarrow R-CH_2-OH + LiOH$$

Alkylation of Carboxylic Acids to Form Ketones

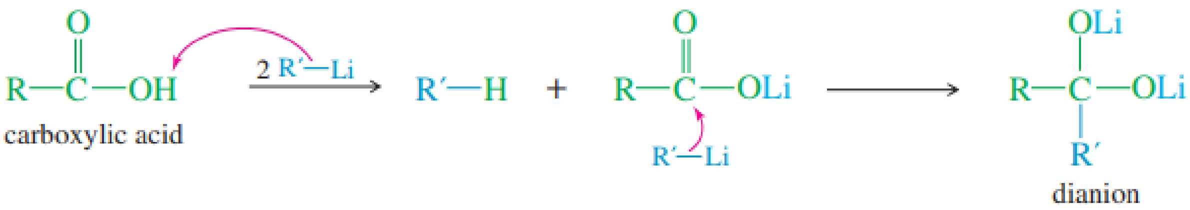
Carboxylic acids react with two equivalents of an organolithium reagent to give ketones.

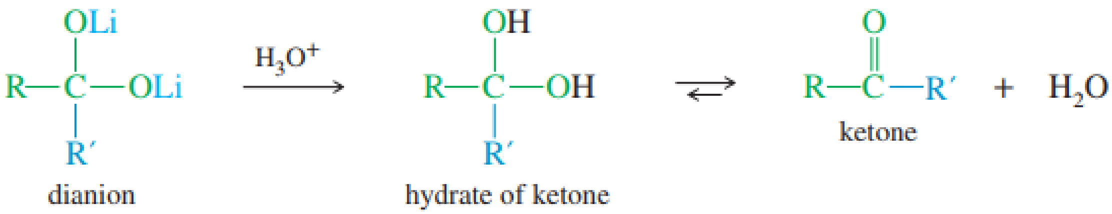


Example



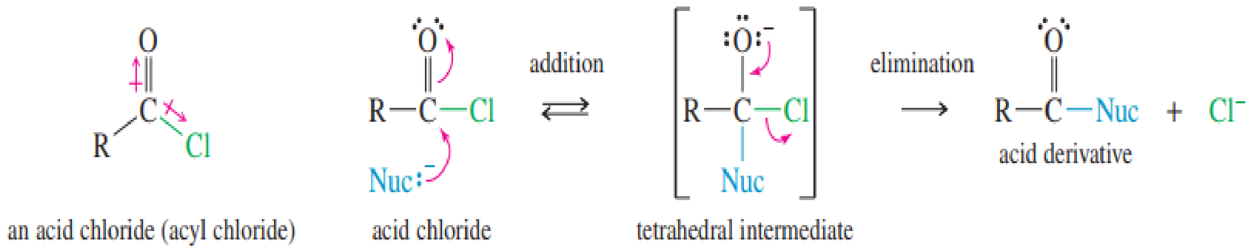
MECHANISM of Alkylation

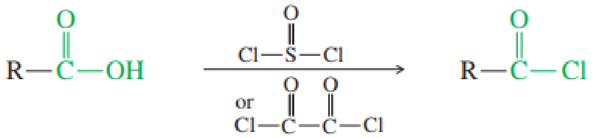




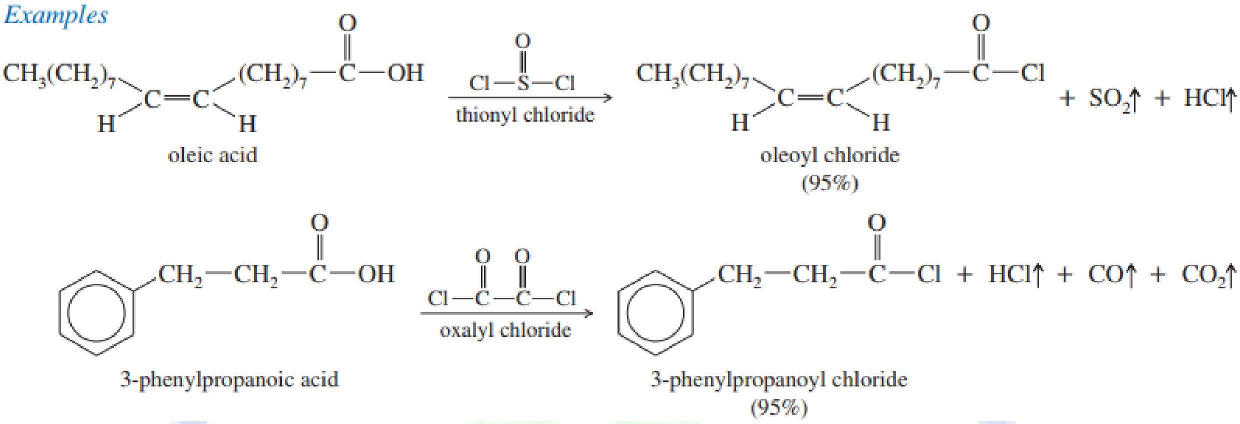
Synthesis and Use of Acid Chlorides

Halide ions are excellent leaving groups for nucleophilic acyl substitution. Therefore, acyl halides are useful intermediates for making acid derivatives. In particular, acid chlorides (acyl chlorides) are easily made and are commonly used as an activated form of a carboxylic acid. Both the carbonyl oxygen and the chlorine atom withdraw electron density from the acyl carbon atom, making it strongly electrophilic. Acid chlorides react with a wide range of nucleophiles, generally through the addition–elimination mechanism of nucleophilic acyl substitution.

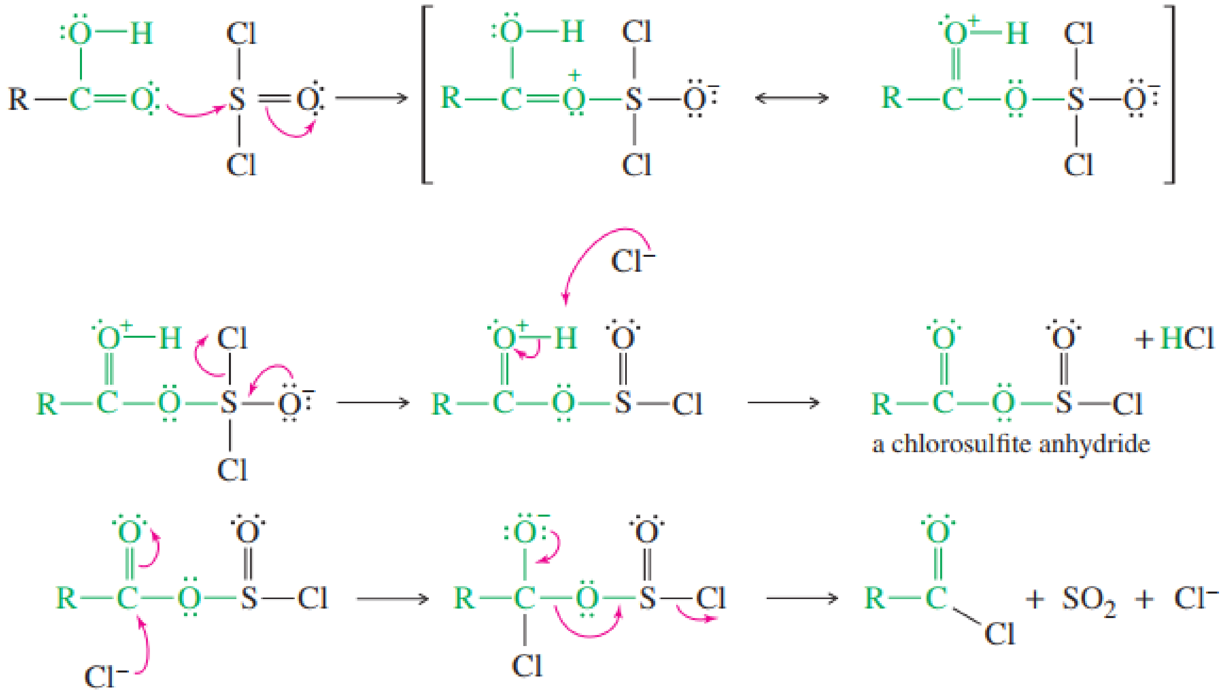




Examples



MECHANISM of Synthesis Acid Chlorides



Reactions of Carboxylic Acids