

CH 310 N

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LECTURE 12

Textbook Assignment: Chapter 16 Continue

Homework (for credit): POW 6 posted

Today's Topics: Carboxylic Acids

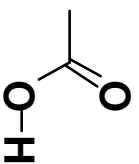
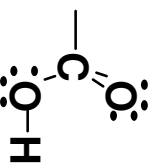
Notice & Announcements:

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Carboxylic Acids

Structure

- The functional group of a carboxylic acid is a carboxyl group



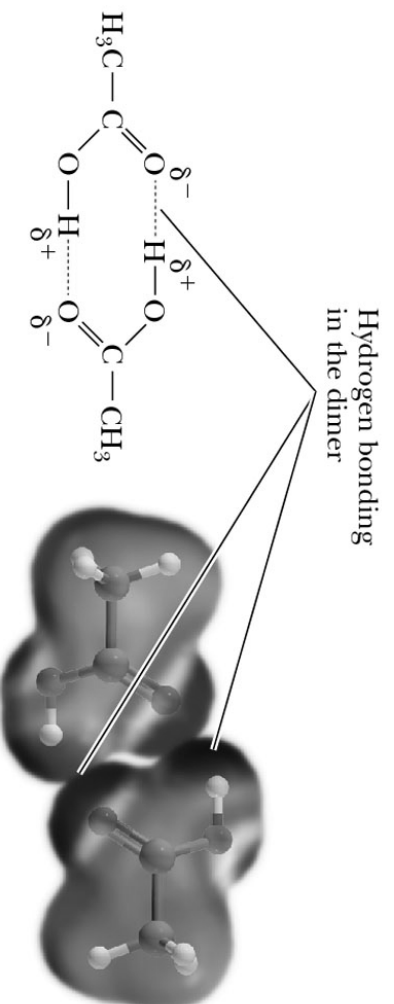
Alternative representations for a carboxyl group

- the general formula for an aliphatic carboxylic acid is RCOOH; that for an aromatic carboxylic acid is ArCOOH

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Physical Properties

- In the liquid and solid states, carboxylic acids are associated by hydrogen bonding into dimeric structures



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Physical Properties

- Carboxylic acids have significantly **higher boiling points** than other types of organic compounds of comparable molecular weight
 - they are polar compounds and form very strong intermolecular hydrogen bonds

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Physical Properties

- Carboxylic acids are more **soluble in water than alcohols**, ethers, aldehydes, and ketones of comparable molecular weight
 - they form hydrogen bonds with water molecules through their C=O and OH groups

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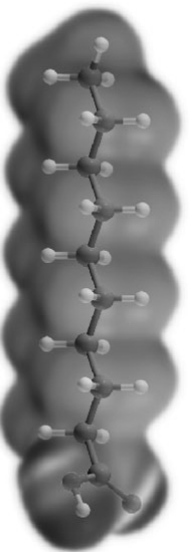
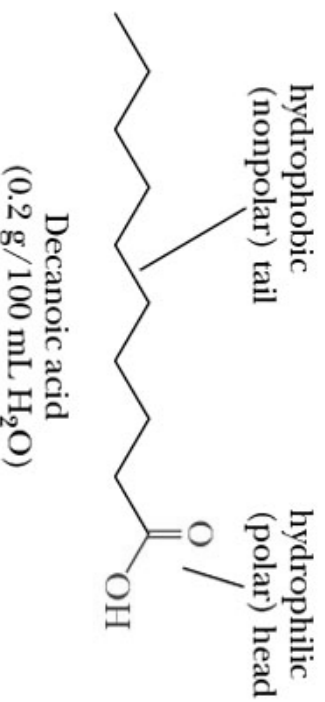
Physical Properties

Structure	Name	Molecular Weight (g/mol)	Boiling Point (°C)	Solubility (g/100 g H ₂ O)
CH ₃ COOH	Acetic acid	60.1	118	Infinite
CH ₃ CH ₂ CH ₂ OH	1-Propanol	60.1	97	Infinite
CH ₃ CH ₂ CHO	Propanal	58.1	48	16
.....				
CH ₃ (CH ₂) ₂ COOH	Butanoic acid	88.1	163	Infinite
CH ₃ (CH ₂) ₃ CH ₂ OH	1-Pentanol	88.1	137	2.3
CH ₃ (CH ₂) ₃ CHO	Pentanal	86.1	103	Slight
.....				
CH ₃ (CH ₂) ₄ COOH	Hexanoic acid	116.2	205	1.0
CH ₃ (CH ₂) ₅ CH ₂ OH	1-Heptanol	116.2	176	0.2
CH ₃ (CH ₂) ₅ CHO	Heptanal	114.1	153	0.1

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Physical Properties

water solubility decreases as the relative size of the hydrophobic portion of the molecule increases

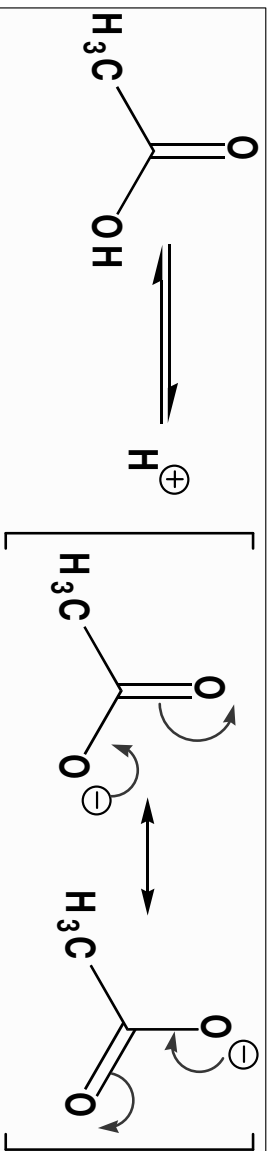


Electrostatic potential map

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Acidity

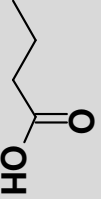
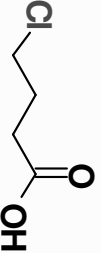
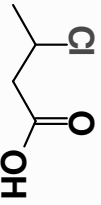
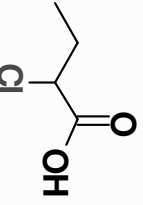
- Carboxylic acids are **weak acids**
 - values of pK_a for most aliphatic and aromatic carboxylic acids fall within the range 4 to 5
- The greater acidity of carboxylic acids relative to alcohols (both compounds that contain an OH group) is due to resonance stabilization of the carboxylate anion



Molecular Structure and Acidity


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– the operation of the inductive effect in the acidity of halogen substituted carboxylic acids is also observed:

 <p>Butanoic acid pK_a 4.82</p>	 <p>4-Chlorobutanoic acid pK_a 4.52</p>	 <p>3-Chlorobutanoic acid pK_a 3.98</p>	 <p>2-Chlorobutanoic acid pK_a 2.83</p>
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Acidity

–electron-withdrawing substituents near the carboxyl group increase acidity through their inductive effect

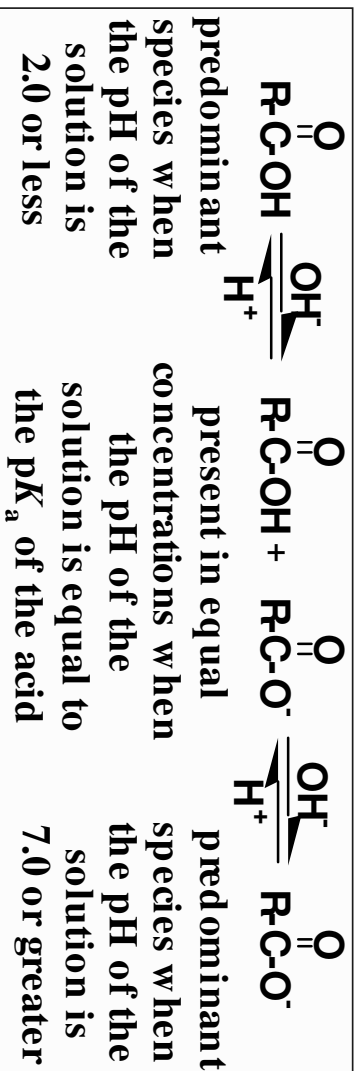
Formula:	CH ₃ COOH	ClCH ₂ COOH	Cl ₂ CHCOOH	Cl ₃ CCOOH
Name:	Acetic acid	Chloroacetic acid	Dichloroacetic acid	Trichloroacetic acid
pK _a :	4.76	2.86	1.48	0.70
Increasing acid strength 				



Note: the pK_a scale is a logarithmic scale

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the form of a carboxylic acid present in aqueous solution depends on the pH of the solution:



$$\text{pH} = pK_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$$

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For organic acids in equilibrium:



Henderson-Hasselbalch equation:

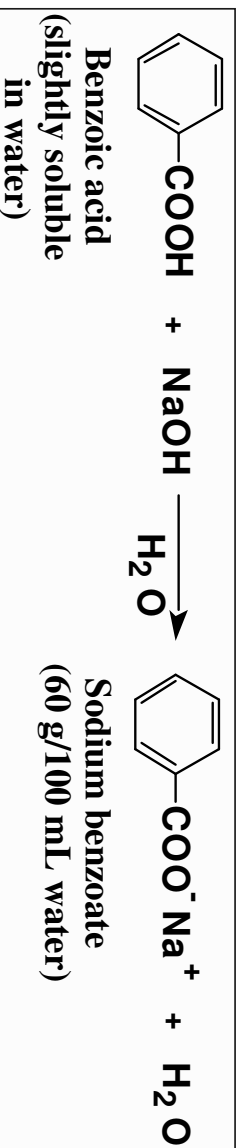
$$pH = pK_a + \log_{10} \frac{[A^-]}{[HA]}$$

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Reaction with Bases

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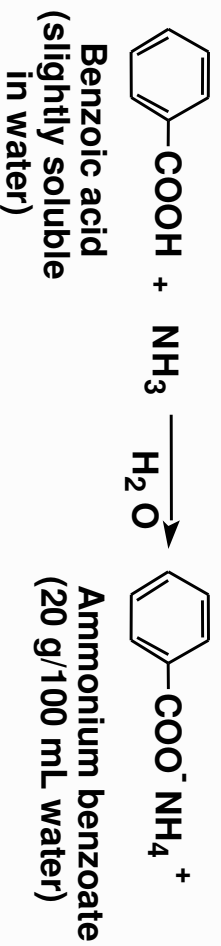
Carboxylic acids, whether soluble or insoluble in water, react with NaOH, KOH, and other strong bases to give water-soluble salts



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Reaction with Bases

- They also form water-soluble salts with ammonia and amines

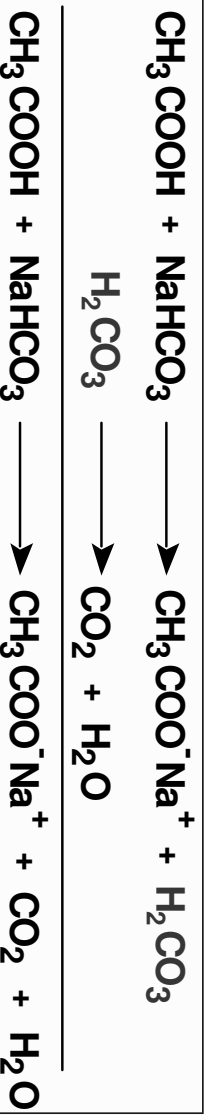


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Reaction with Bases

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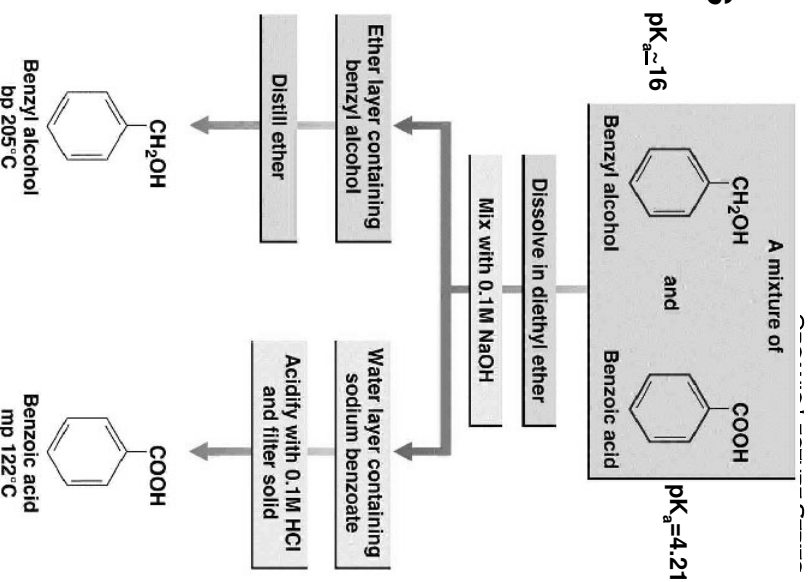
- Carboxylic acids react with sodium bicarbonate and sodium carbonate to form water-soluble salts and carbonic acid
 - carbonic acid, in turn, breaks down to carbon dioxide and water



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Exploiting pKa differences

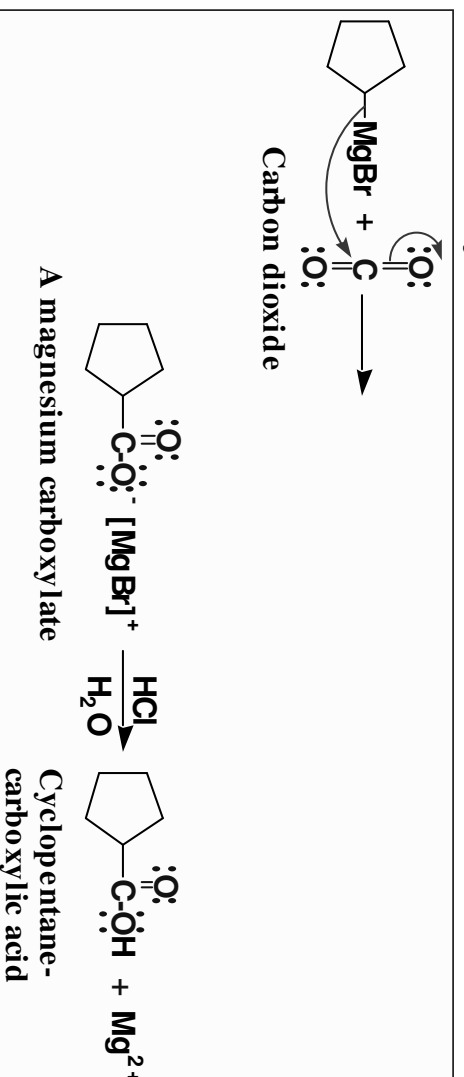
- Reaction with bases
 - the acid-base properties of carboxylic acids allow an easy separation of carboxylic acids from water-insoluble nonacidic compounds



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Preparation

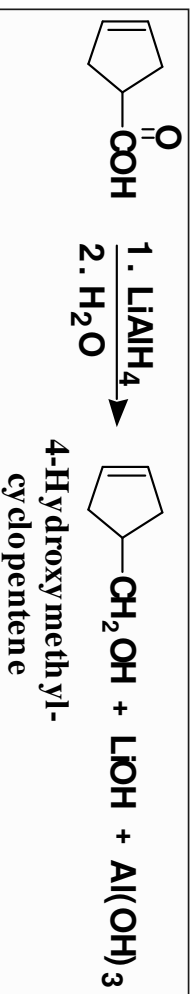
- Carbonation of Grignard reagents
 - treatment of a Grignard reagent with carbon dioxide followed by acidification gives a carboxylic acid



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Reduction

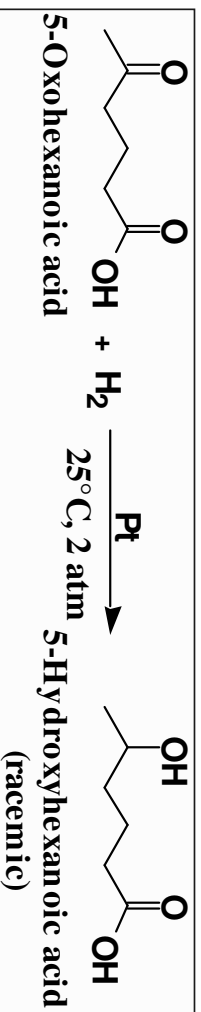
- The carboxyl group is very resistant to reduction
 - it is not affected by catalytic hydrogenation under conditions that easily reduce aldehydes and ketones to alcohols, and reduce alkenes and alkynes to alkanes; it is not reduced by NaBH_4
- **Lithium aluminum hydride reduces a carboxyl group to a 1° alcohol**
 - reduction is carried out in diethyl ether, THF, or other nonreactive, aprotic solvent



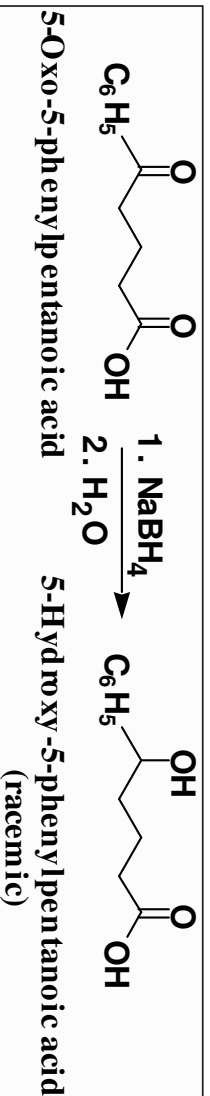
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Selective Reduction

- carboxyl groups are not affected by catalytic reduction under conditions that reduce aldehydes and ketones



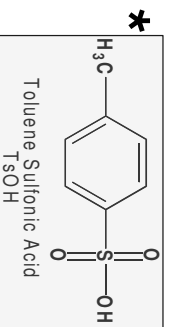
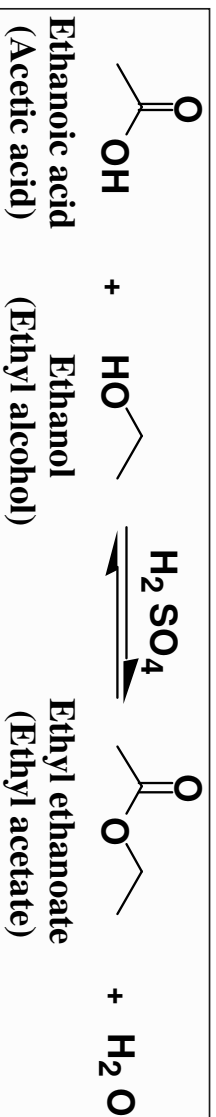
- nor are carboxyl groups reduced by NaBH_4



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Fischer Esterification

- Esters can be prepared by treating a carboxylic acid with an alcohol in the presence of an acid catalyst, commonly H_2SO_4 , ArSO_3H^* , or gaseous HCl



Psst...
He will ask
this

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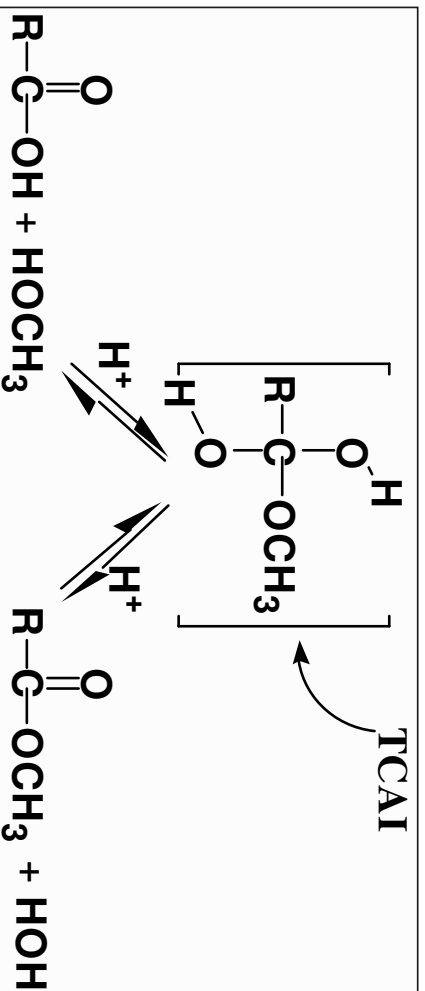
Fischer Esterification

Fischer esterification is an equilibrium reaction

- by careful control of experimental conditions, it is possible to prepare esters in high yield
- if the alcohol is inexpensive relative to the carboxylic acid, it can be used in excess to drive the equilibrium to the right
- alternatively, water can be removed by azeotropic distillation and a Dean-Stark trap

Fischer Esterification

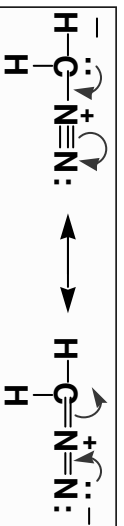
– a key intermediate in Fischer esterification is the tetrahedral carbonyl addition intermediate formed by addition of ROH to the C=O group



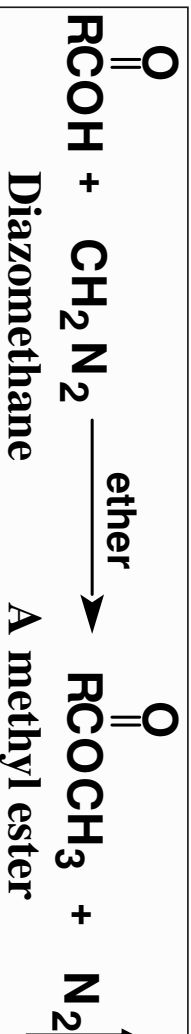
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Diazomethane

- Diazomethane, CH_2N_2 (a methylating agent)
 - a potentially explosive, toxic, yellow gas, is best represented as a hybrid of two contributing structures



– treating a carboxylic acid with diazomethane gives a **methyl ester**

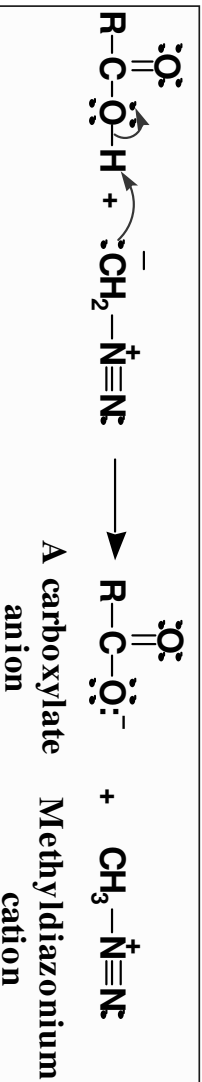


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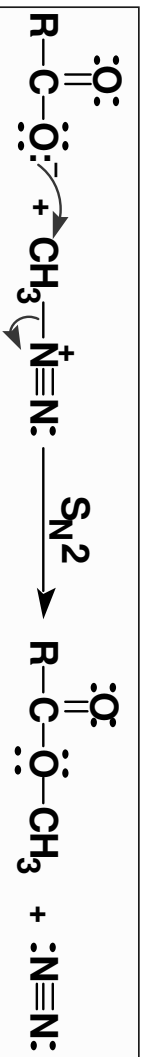
Diazomethane

- Esterification occurs in two steps

Step 1: proton transfer to diazomethane



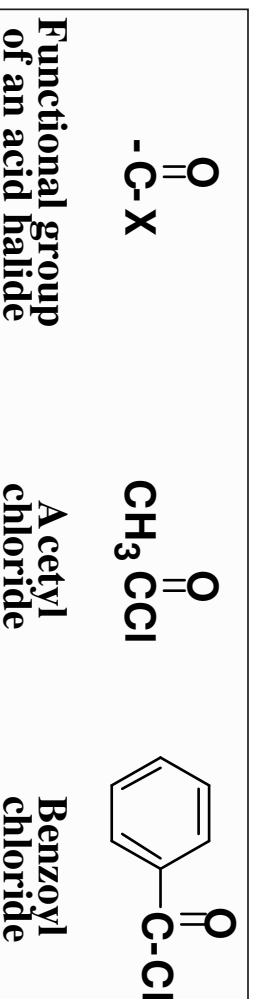
Step 2: nucleophilic displacement of N_2



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Acid Chlorides

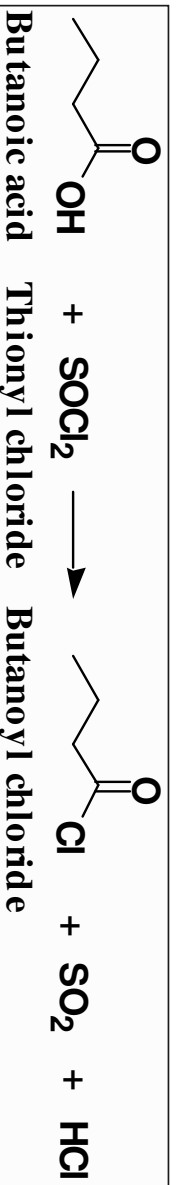
- The functional group of an acid halide is a carbonyl group bonded to a halogen atom
 - among the acid halides, acid chlorides are by far the most common and the most widely used



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Acid Chlorides

—acid chlorides are most often prepared by treating a carboxylic acid with **thionyl chloride**

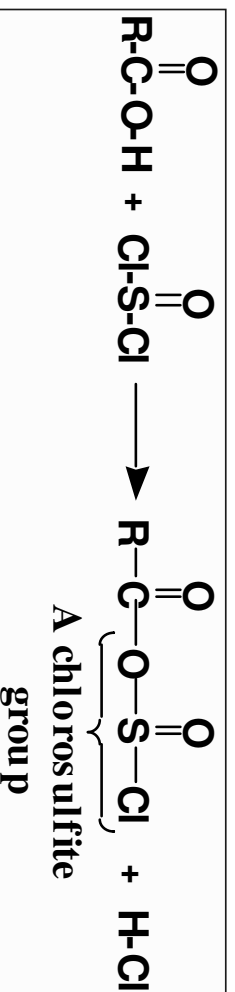


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Acid Chlorides

- The mechanism for this reaction is divided into two steps.

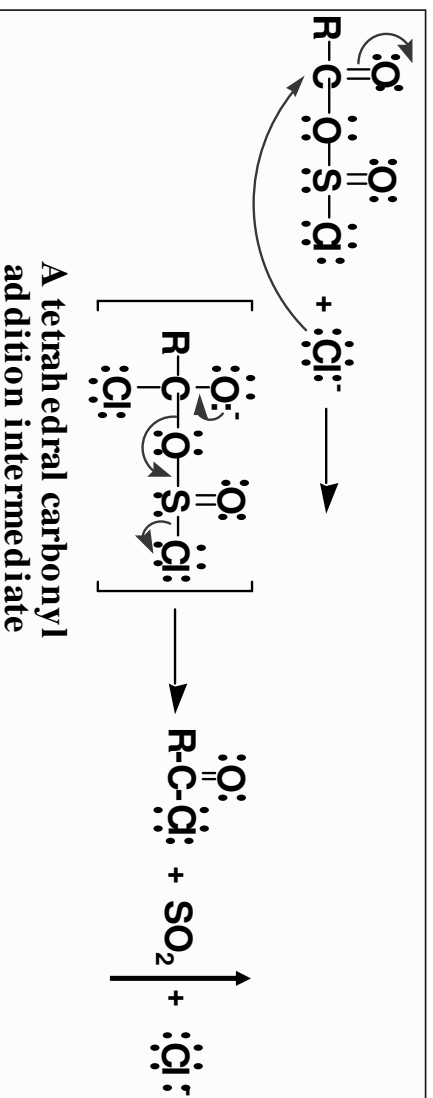
Step 1: reaction with SOCl_2 transforms OH, a poor leaving group, into a chlorosulfite group, a good leaving group



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Acid Chlorides

Step 2: attack of chloride ion gives a tetrahedral carbonyl addition intermediate, which collapses to give the acid chloride



Note: the reaction is irreversible