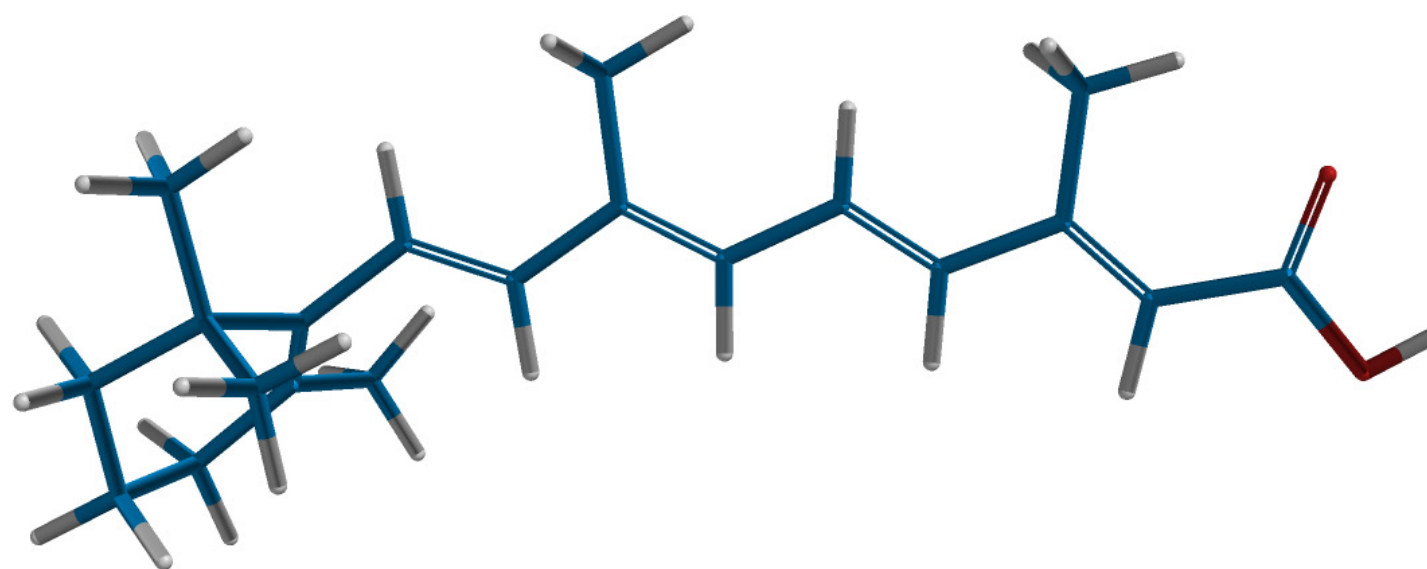


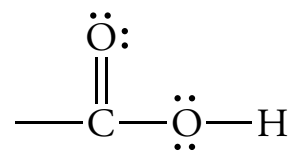
20

# CARBOXYLIC ACIDS

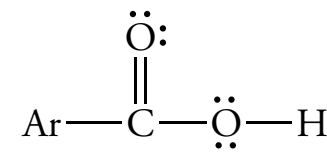
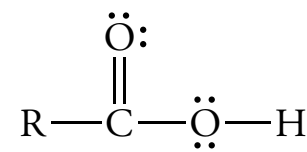


RETANOIC ACID

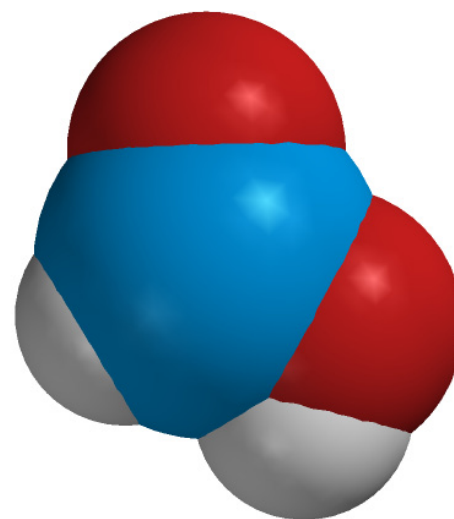
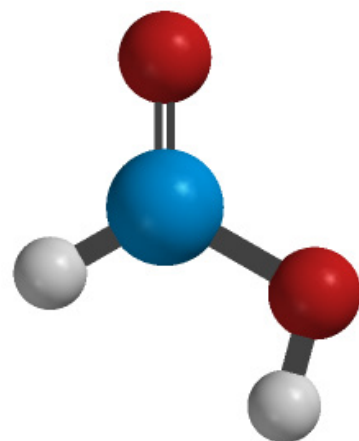
## 20.1 CARBOXYLIC ACIDS AND ACYL GROUPS



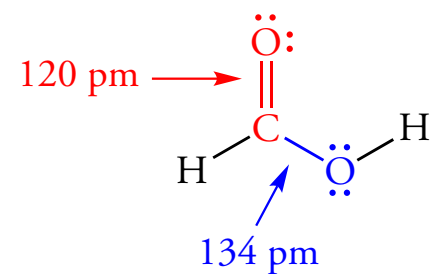
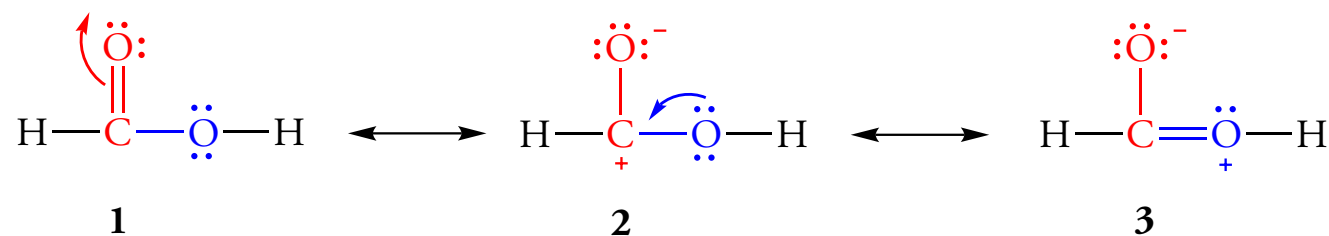
carboxyl group



carboxylic acids

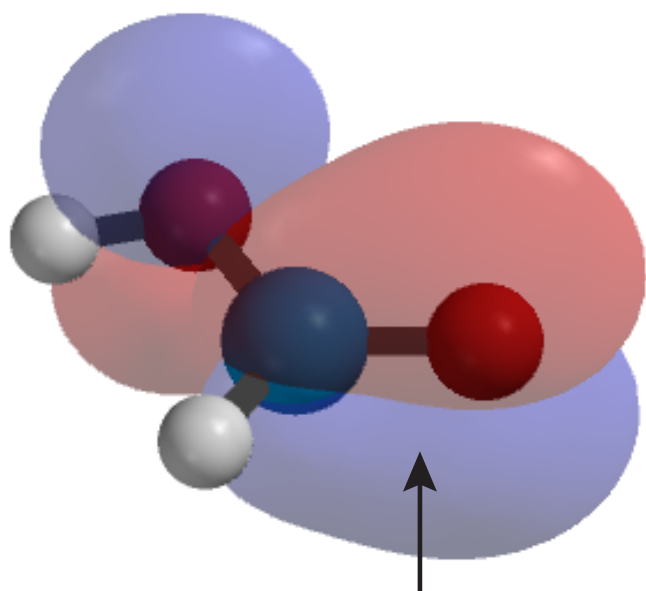


methanoic acid



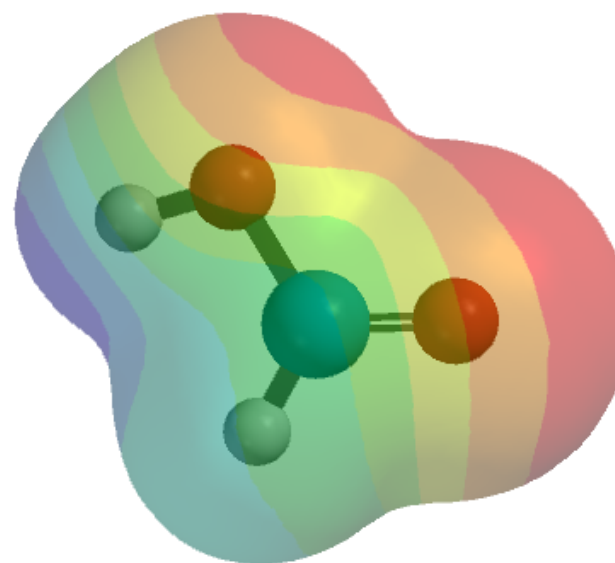
## Figure 20.1 Bonding in Carboxylic Acids

(a) Lowest energy bonding orbital in methanoic acid (formic acid)



The  $\pi$  bond is formed by overlap of the 2p orbitals of carbon and oxygen.

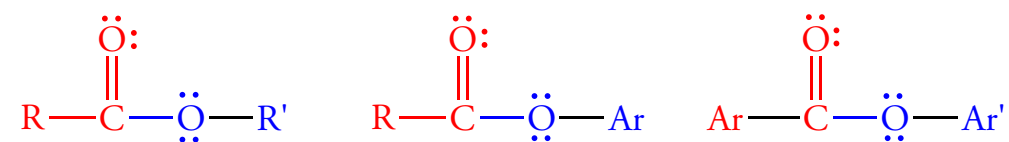
(b) Electron distribution in methanoic acid



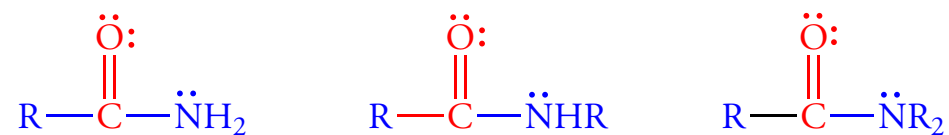
Regions colored red have a partial negative charge (at the carboxyl oxygens) and regions colored blue have a partial positive charge (at the hydroxyl hydrogen and carbonyl carbon).

# 20.1 CARBOXYLIC ACIDS AND ACYL GROUPS

## The Acyl Group and Carboxylic Acid Derivatives



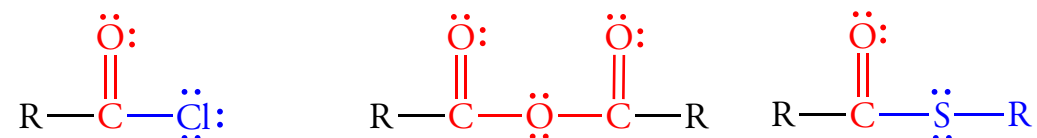
examples of esters (acyl groups shown in red)



primary amide

secondary amide

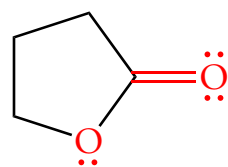
tertiary amide



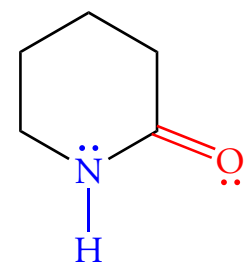
acid chloride

acid anhydride

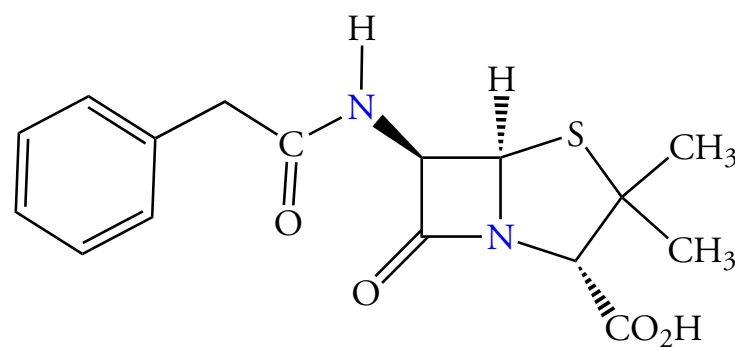
thioester



lactone  
(a cyclic ester)



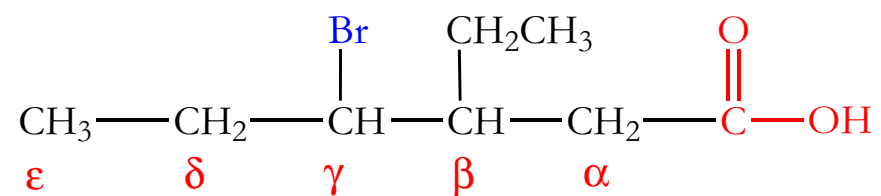
lactam  
(a cyclic amide)



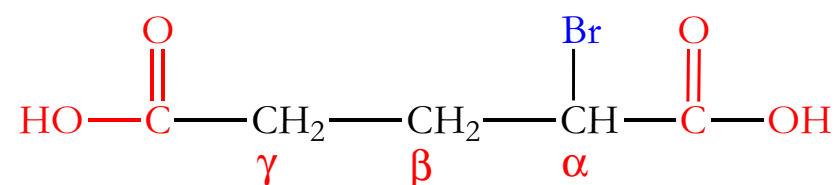
penicillin G

## 20.2 NOMENCLATURE OF CARBOXYLIC ACIDS

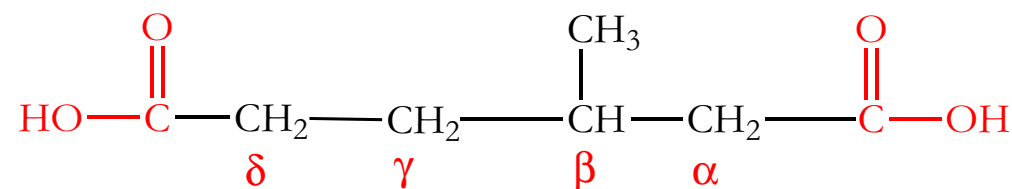
### Common Names of Carboxylic Acids



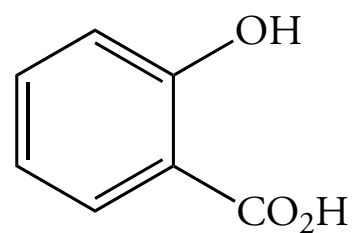
$\gamma$ -bromo- $\beta$ -ethylcaproic acid



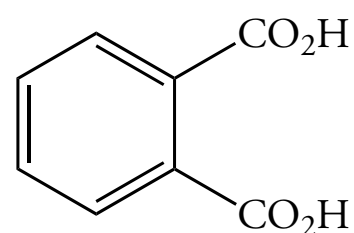
$\alpha$ -bromoglutaric acid



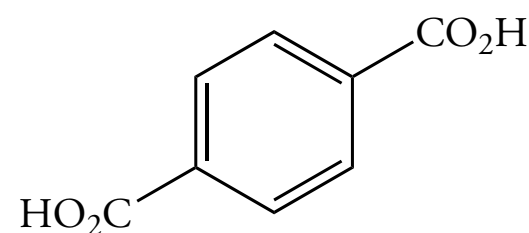
$\beta$ -methyladipic acid



salicylic acid



phthalic acid



terephthalic acid

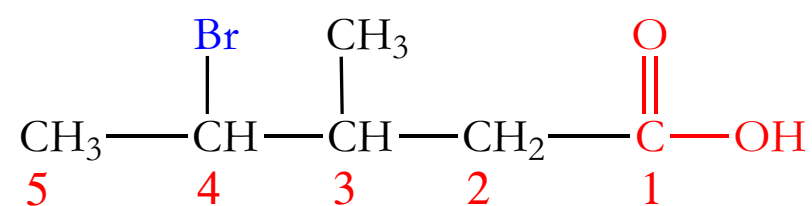
**Table 20.1**  
**Nomenclature of Carboxylic Acids**

<i>Formula</i>	<i>Common Name</i>	<i>IUPAC Name</i>
$\text{HCO}_2\text{H}$	formic acid	methanoic acid
$\text{CH}_3\text{CO}_2\text{H}$	acetic acid	ethanoic acid
$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$	propionic acid	propanoic acid
$\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{H}$	butyric acid	butanoic acid
$\text{CH}_3(\text{CH}_2)_3\text{CO}_2\text{H}$	valeric acid	pentanoic acid
$\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$	caproic acid	hexanoic acid
$\text{CH}_3(\text{CH}_2)_6\text{CO}_2\text{H}$	caprylic acid	octanoic acid
$\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2\text{H}$	lauric acid	dodecanoic acid
$\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}$	myristic	tetradecanoic acid
$\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$	palmitic	hexadecanoic acid
$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$	stearic	octadecanoic acid

## 20.2 NOMENCLATURE OF CARBOXYLIC ACIDS

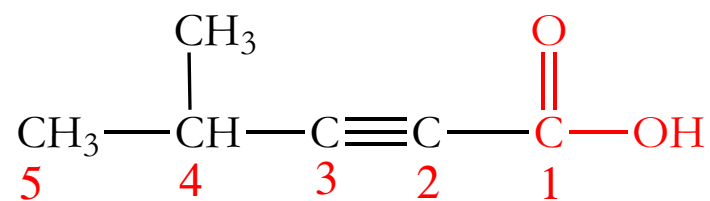
### IUPAC Names of Carboxylic Acids

1. Name the longest continuous carbon chain containing the carboxyl carbon atom as the parent chain. Replace the final *-e* of the parent hydrocarbon by the ending *-oic acid*. Table 20.1 gives examples of IUPAC names of unsubstituted carboxylic acids.
2. Number the parent chain by assigning the number 1 to the carboxyl carbon atom. Do *not* add the number "1" to the name to indicate the position of the carboxyl carbon because it must be located at the end of the chain. Add the names and locations of any substituents as prefixes to the parent name.



4-bromo-3-methylpentanoic acid

3. The carboxylic acid group has a higher priority than double or triple bonds. To name a carboxylic acid that contains a double or triple bond, replace the final *-e* of the name of the parent alkene or alkyne name with the suffix *-oic acid*. Indicate the position of the multiple bond with a prefix.

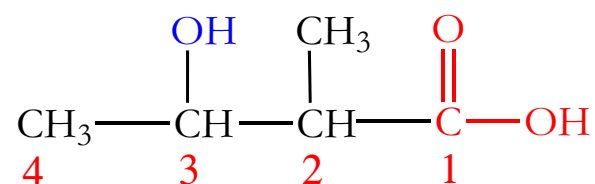


4-methyl-2-pentynoic acid

## 20.2 NOMENCLATURE OF CARBOXYLIC ACIDS

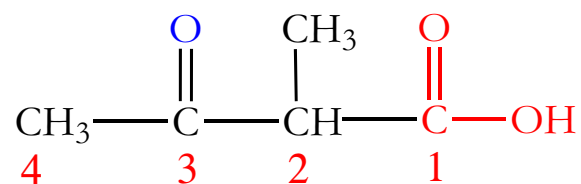
### IUPAC Names of Carboxylic Acids

4. The carboxylic acid functional group has a higher priority than aldehyde, ketone, halogen, hydroxyl, and alkoxy groups. Indicate the names and locations of these groups with prefixes to the name of the parent carboxylic acid.



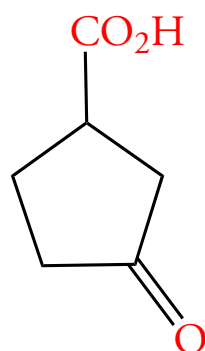
3-hydroxy-2-methylbutanoic acid

5. If a carboxylic acid contains an aldehyde or ketone, the names of the carbonyl group is *-oxo*. The priority order is aldehyde > ketone.

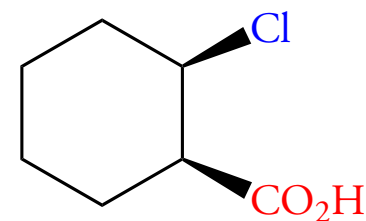


2-methyl-3-oxobutanoic acid

6. Name compounds that have a  $\text{—COOH}$  group bonded to a cycloalkane ring as derivatives of the cycloalkane with the suffix *carboxylic acid*. The ring atom to which the carboxyl group is attached is C-1. Do *not* include this number in the name.



3-oxocyclopentanecarboxylic acid



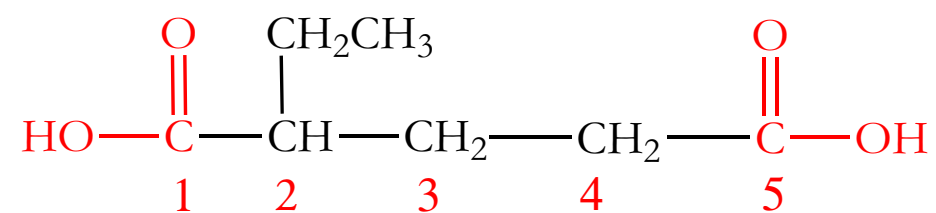
*cis*-2-chlorocyclohexanecarboxylic acid



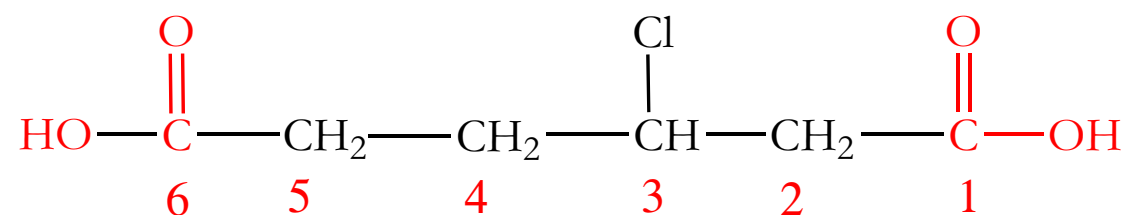
## 20.2 NOMENCLATURE OF CARBOXYLIC ACIDS

### IUPAC Names of Carboxylic Acids

7. Name dicarboxylic acids by adding the suffix *dioic acid* to the name the parent alkane that contains both carboxylic acid groups. Number the chain starting with the carboxyl carbon closest to the first substituent.



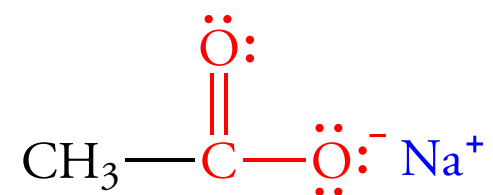
2-ethylpentanedioic acid



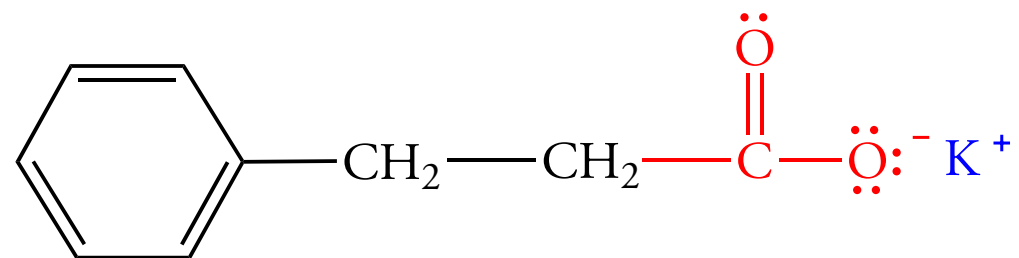
3-chlorohexanedioic acid

## 20.1 CARBOXYLIC ACIDS AND ACYL GROUPS

### Names of Carboxylate Anions



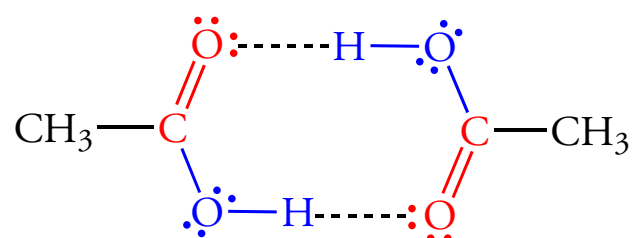
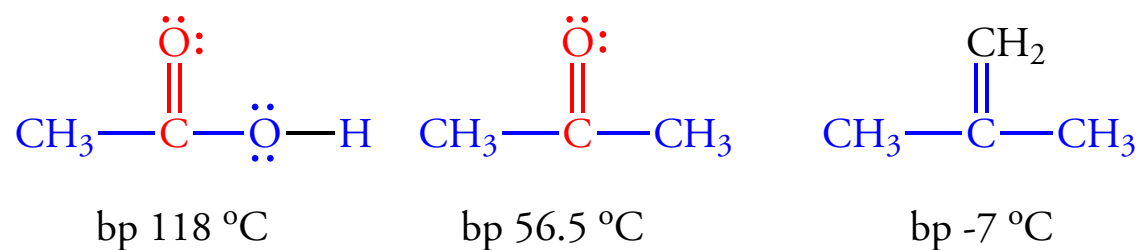
sodium ethanoate  
(sodium acetate)



potassium 3-phenylpropanoate  
(potassium  $\beta$ -phenylpropionate)

## 20.3 PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

### Boiling Points



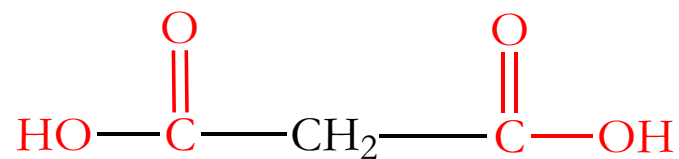
hydrogen-bonded dimer of acetic acid

**Table 20.2**  
**Boiling Points of Carboxylic Acids**

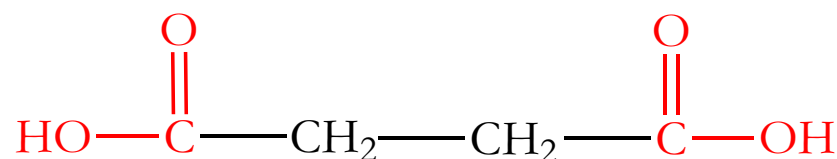
<i>IUPAC Name</i>	<i>Common Name</i>	<i>Boiling Point, °C</i>
methanoic acid	formic acid	101
ethanoic acid	acetic acid	118
propanoic acid	propionic acid	141
butanoic acid	butyric acid	164
2-methylpropanoic acid	isobutyric acid	155
pentanoic acid	valeric acid	186
3-methylbutanoic acid	isovaleric acid	177
2,2-dimethylpropanoic acid	pivalic acid	164
hexanoic acid	caproic acid	205
octanoic acid	caprylic acid	239
decanoic acid	capric	270
dodecanoic acid	lauric acid	299

## 20.3 PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

### Melting Points



malonic acid  
mp 136 °C



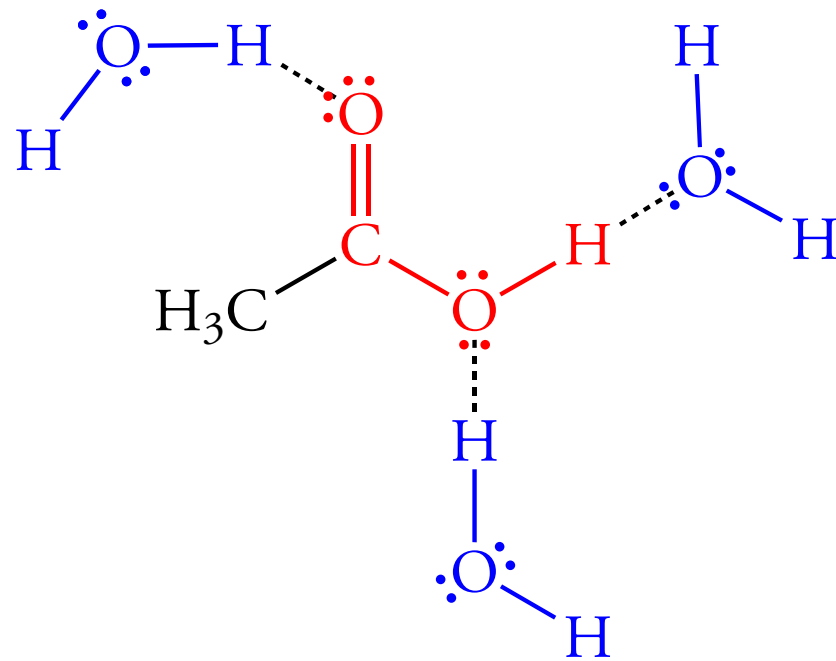
succinic acid  
mp 185 °C

**Table 20.2**  
**Melting Points of Carboxylic Acids**

<i>Number of Carbon Atoms</i>	<i>IUPAC Name</i>	<i>Common Name</i>	<i>Melting Point, °C</i>
10	decanoic acid	capric acid	31.3
12	dodecanoic acid	lauric acid	43.2
14	tetradecanoic acid	myristic acid	54.4
16	hexadecanoic acid	myristic acid	62.8
18	octadecanoic acid	isobutyric acid	69.9
20	eicosanoic acid	arachidic acid	75.4
22	docosanoic acid	behenic acid	79.9
24	tetracosanoic acid	lignoceric acid	84.2
26	hexacosanoic acid	ceratoic acid	87.7

## 20.3 PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

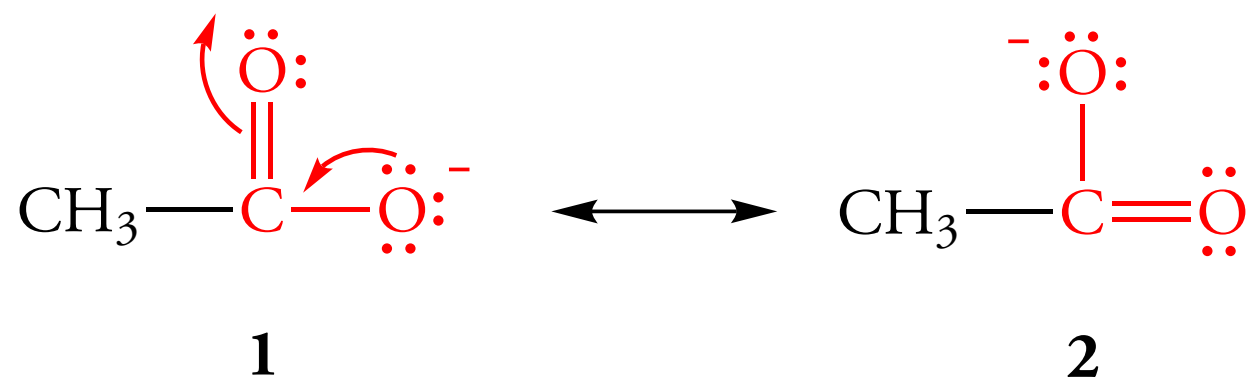
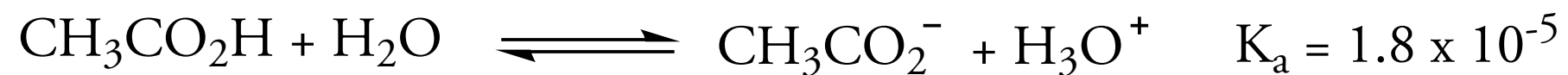
### Solubilities



hydrogen bonds between acetic acid and water in aqueous solution

## 20.4 ACIDITY OF CARBOXYLIC ACIDS

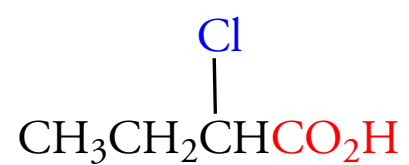
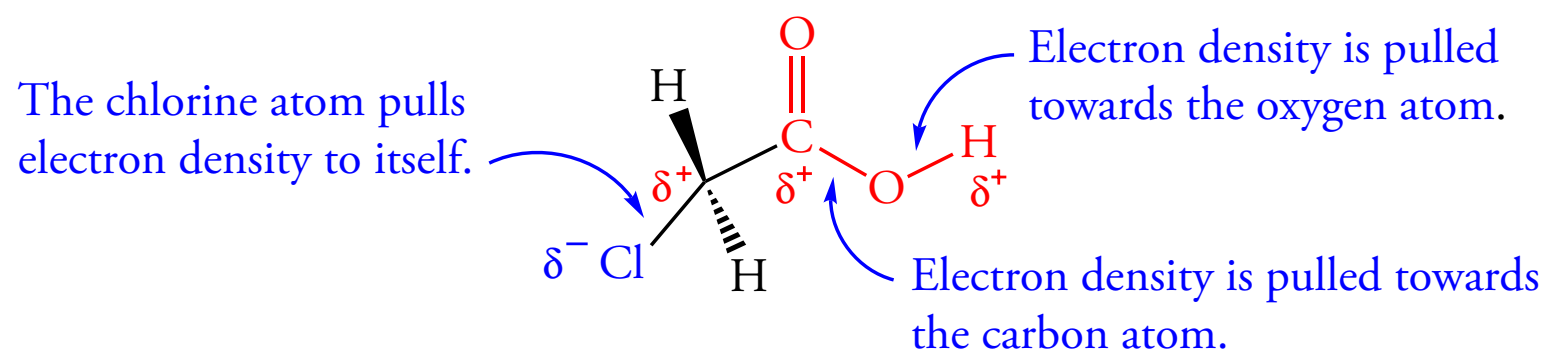
### Resonance Stabilization of the Carboxylate Ion



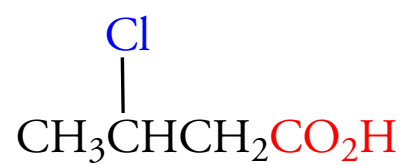
Resonance structures of acetate ion

## 20.4 ACIDITY OF CARBOXYLIC ACIDS

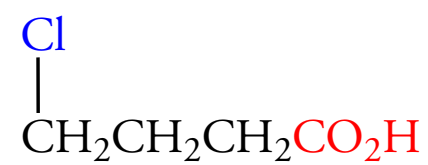
### Inductive Effect on Acidity



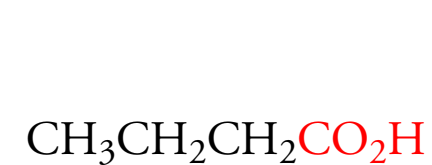
pK<sub>a</sub> 2.84



pK<sub>a</sub> 4.06



pK<sub>a</sub> 4.52



pK<sub>a</sub> 4.72

**Table 20.4**  
**pK<sub>a</sub> Values of Carboxylic Acids**

<i>IUPAC Name</i>	<i>Formula</i>	<i>pK<sub>a</sub></i>
methanoic acid	HCO <sub>2</sub> H	3.75
ethanoic acid	CH <sub>3</sub> CO <sub>2</sub> H	4.72
propanoic acid	CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> H	4.87
butanoic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H	4.82
2-methylbutanoic acid	(CH <sub>3</sub> ) <sub>2</sub> CHCO <sub>2</sub> H	4.84
pentanoic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> H	4.81
2,2-dimethylpropanoic acid	(CH <sub>3</sub> ) <sub>3</sub> CCO <sub>2</sub> H	5.03
fluoroethanoic acid	FCH <sub>2</sub> CO <sub>2</sub> H	2.59
chloroethanoic acid	ClCH <sub>2</sub> CO <sub>2</sub> H	2.86
bromoethanoic acid	BrCH <sub>2</sub> CO <sub>2</sub> H	2.90
iodoethanoic acid	ICH <sub>2</sub> CO <sub>2</sub> H	3.18
dichloroethanoic acid	Cl <sub>2</sub> CHCO <sub>2</sub> H	1.24
trichloroethanoic acid	Cl <sub>3</sub> CCO <sub>2</sub> H	0.64
trifluoroethanoic acid	F <sub>3</sub> CCO <sub>2</sub> H	0.23
methoxyethanoic acid	CH <sub>3</sub> OCH <sub>2</sub> CO <sub>2</sub> H	3.55
cyanoethanoic acid	CNCH <sub>2</sub> CO <sub>2</sub> H	2.46
nitroethanoic acid	NO <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H	1.72

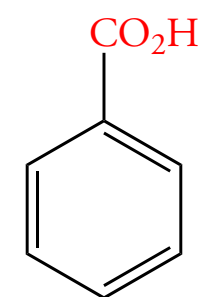
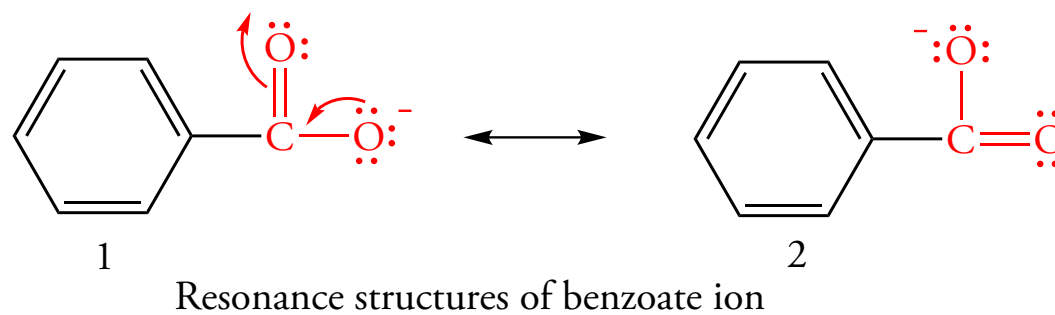
**Table 20.5**  
**pK<sub>a</sub> Values of Dicarboxylic Acids**

<i>IUPAC Name</i>	<i>Formula</i>	<i>pK<sub>a1</sub></i>	<i>pK<sub>a2</sub></i>
oxalic acid	HO <sub>2</sub> CCO <sub>2</sub> H	1.27	4.27
malonic acid	HO <sub>2</sub> CCH <sub>2</sub> CO <sub>2</sub> H	2.85	5.70
succinic acid	HO <sub>2</sub> C(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H	4.35	5.64
glutaric acid	HO <sub>2</sub> C(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> H	4.41	5.41
adipic acid	HO <sub>2</sub> C(CH <sub>2</sub> ) <sub>4</sub> CO <sub>2</sub> H	4.42	5.42
pimelic acid	HO <sub>2</sub> C(CH <sub>2</sub> ) <sub>5</sub> CO <sub>2</sub> H	4.51	5.42
suberic acid	HO <sub>2</sub> C(CH <sub>2</sub> ) <sub>6</sub> CO <sub>2</sub> H	4.52	5.41
azelic acid	HO <sub>2</sub> C(CH <sub>2</sub> ) <sub>7</sub> CO <sub>2</sub> H	4.54	5.41
sebacic acid	HO <sub>2</sub> C(CH <sub>2</sub> ) <sub>8</sub> CO <sub>2</sub> H	4.55	5.40

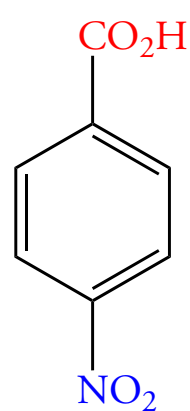


## 20.4 ACIDITY OF CARBOXYLIC ACIDS

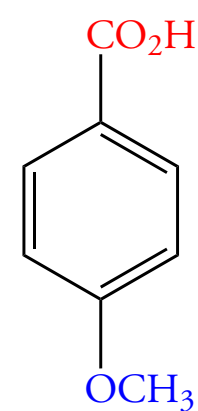
### Acidity of Aromatic Carboxylic Acids



$\text{pK}_a = 4.20$



$\text{pK}_a = 3.42$



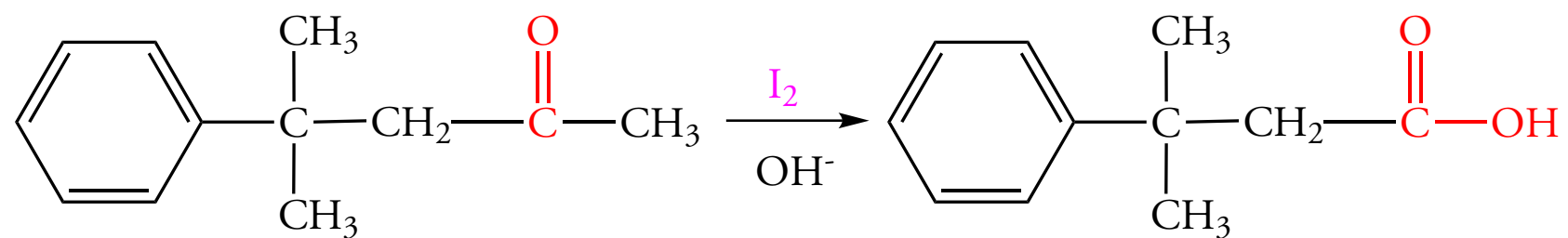
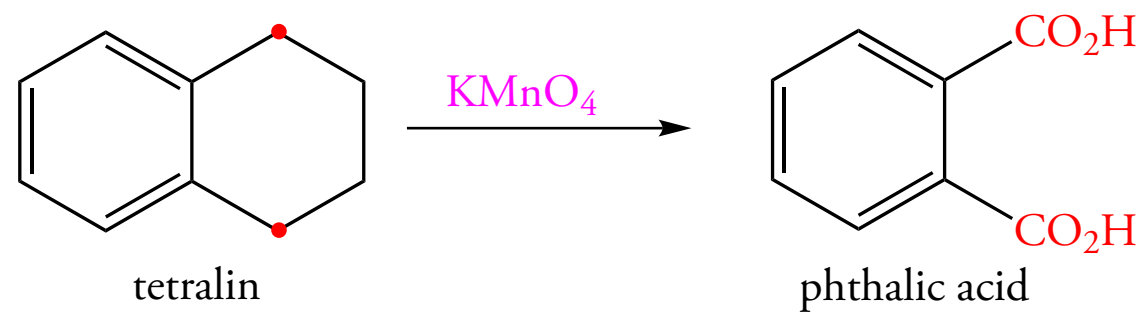
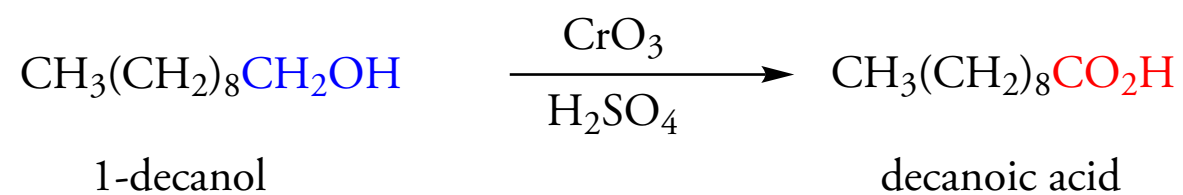
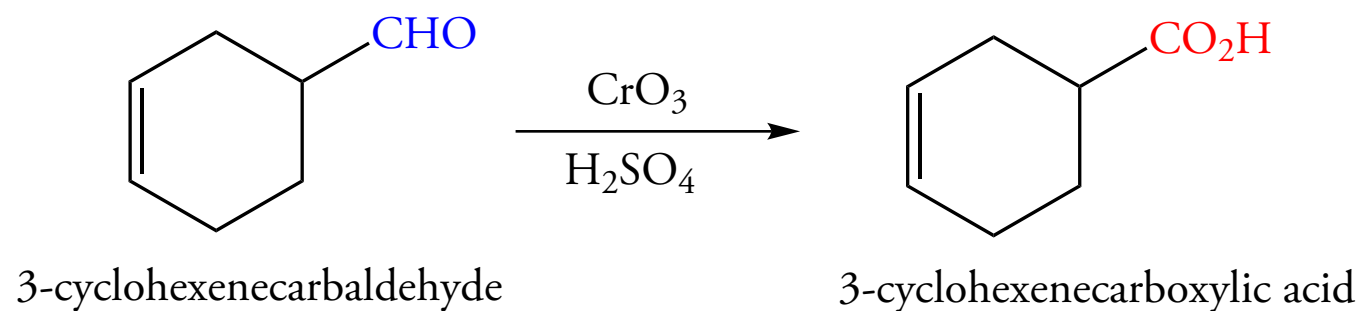
$\text{pK}_a = 4.47$

Table 20.6  
 $\text{pK}_a$  Values of Substituted  
Benzoic Acids

<i>Substituent</i>	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
$\text{CH}_3\text{O}$	4.06	4.10	4.47
$\text{CH}_3$	3.91	4.27	4.37
H	4.20	4.20	4.20
Cl	2.92	3.82	3.98
$\text{NO}_2$	2.17	3.49	3.42

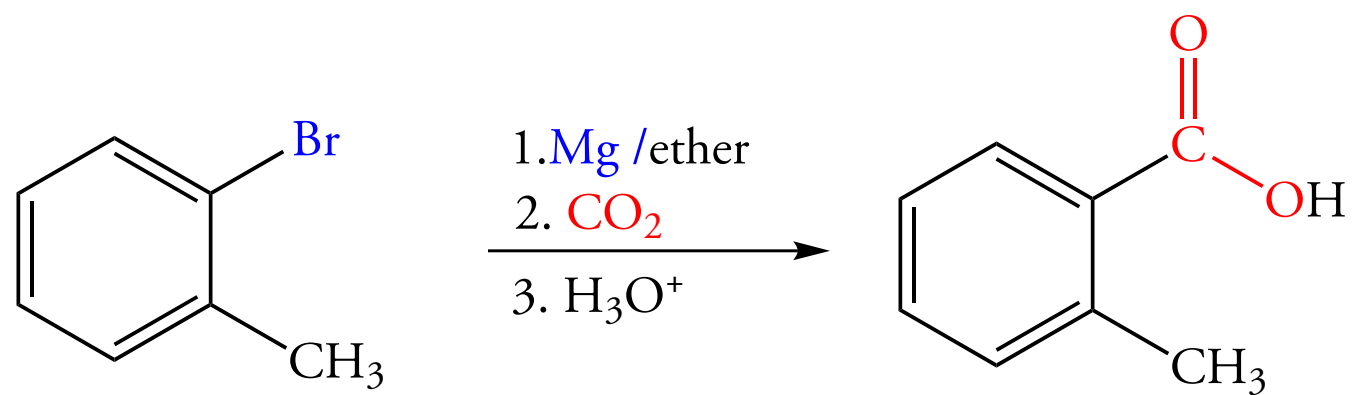
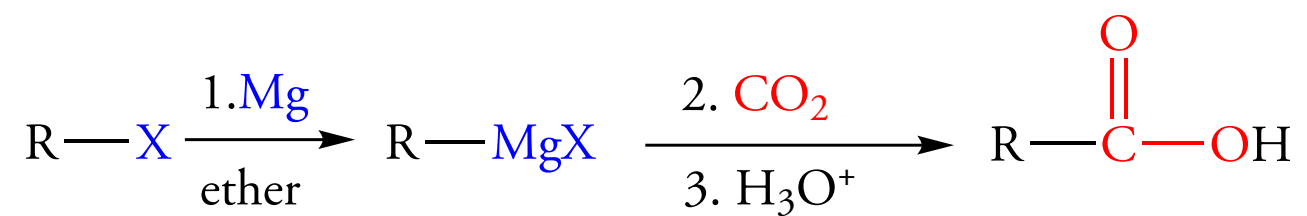
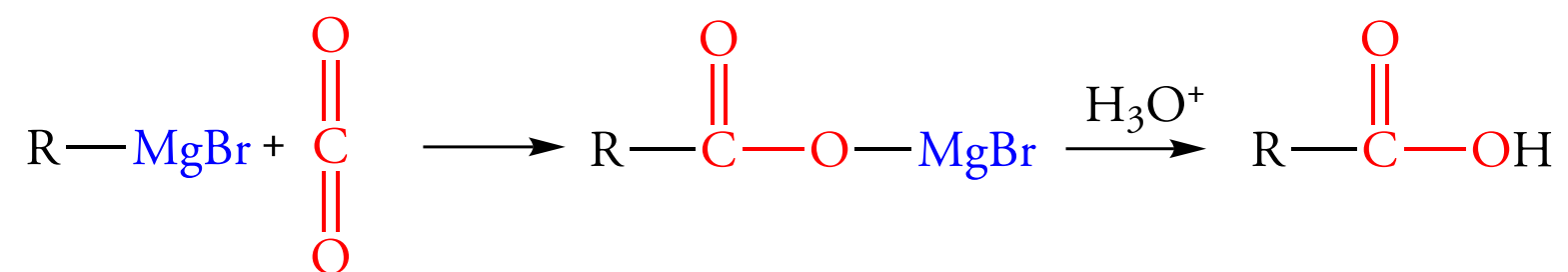
## 20.6 SYNTHESIS OF CARBOXYLIC ACIDS

### Oxidative Methods



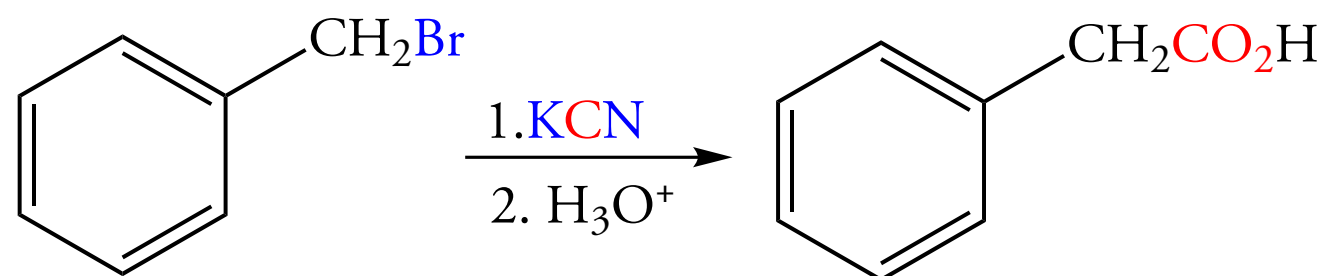
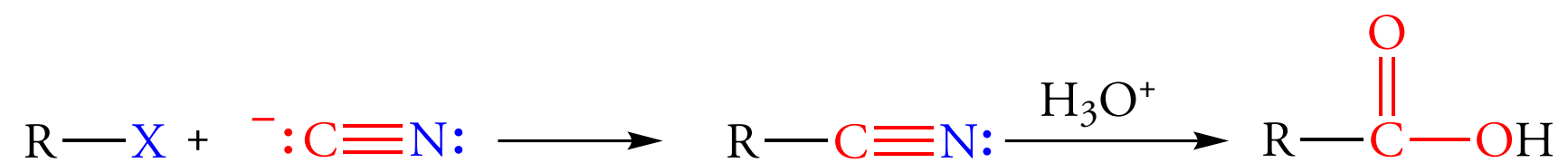
## 20.6 SYNTHESIS OF CARBOXYLIC ACIDS

### Carboxylation of Grignard Reagents



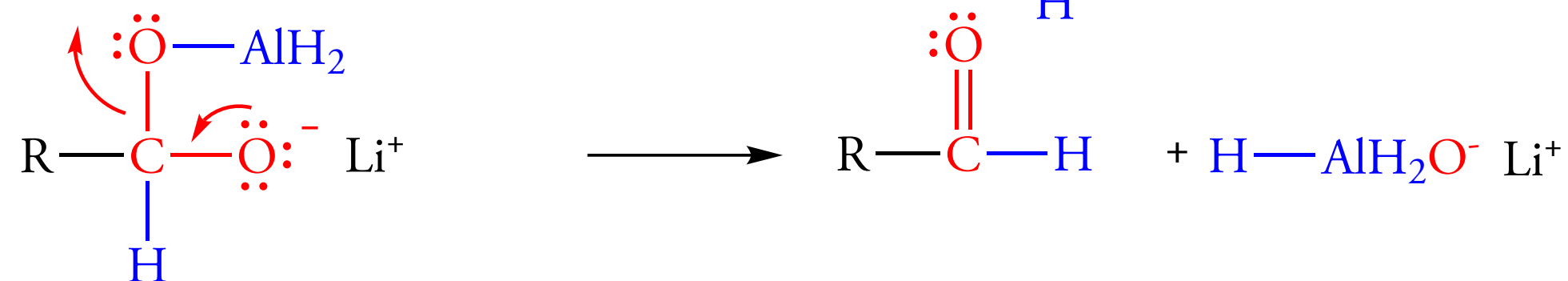
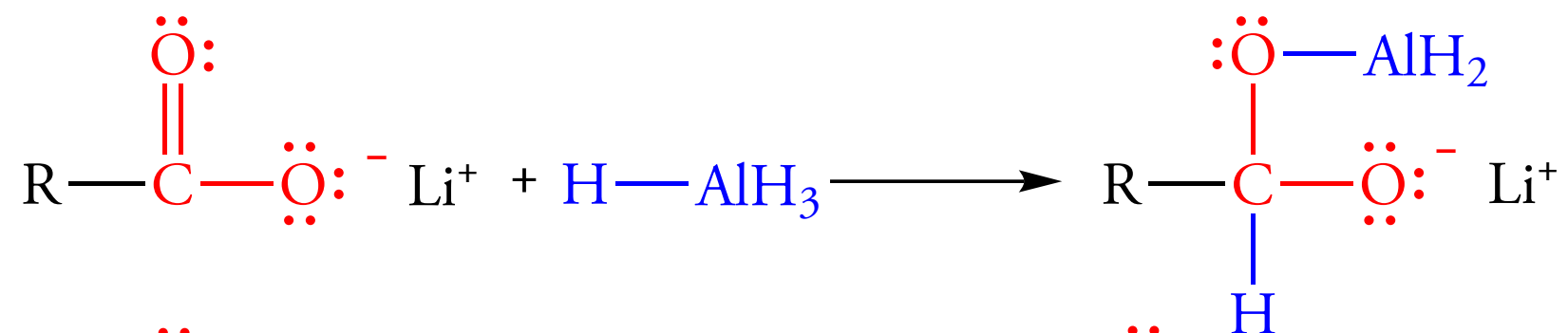
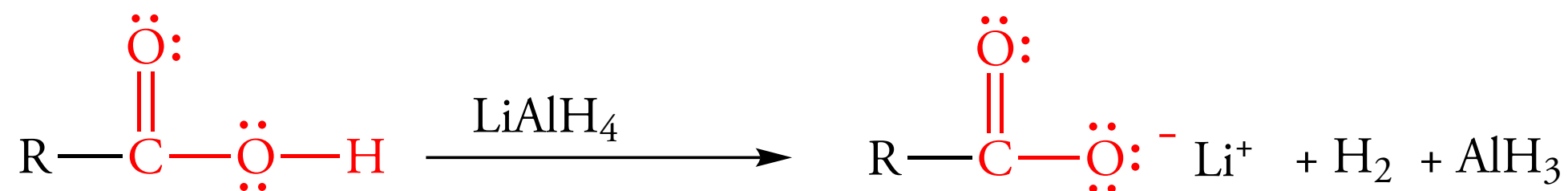
## 20.6 SYNTHESIS OF CARBOXYLIC ACIDS

### Hydrolysis of Nitriles



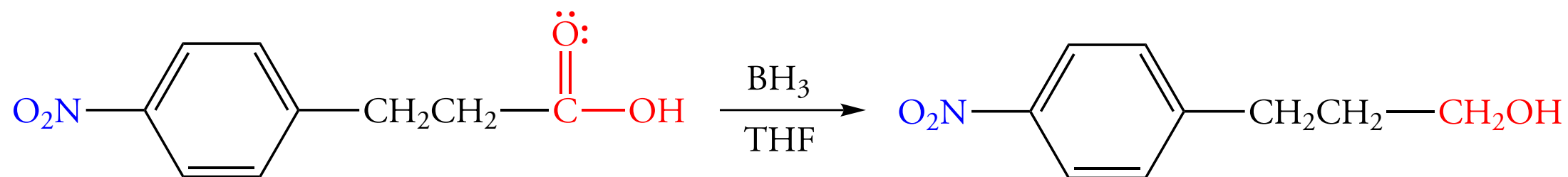
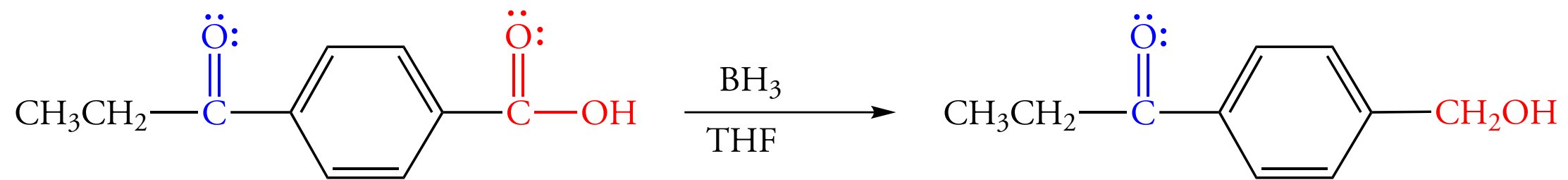
## 20.7 REDUCTION OF CARBOXYLIC ACIDS

### Reduction with Lithium Aluminum Hydride

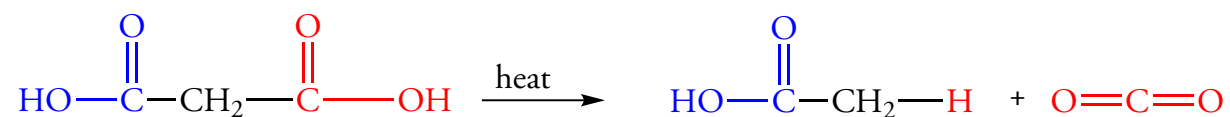
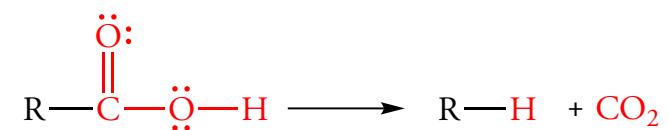


## 20.7 REDUCTION OF CARBOXYLIC ACIDS

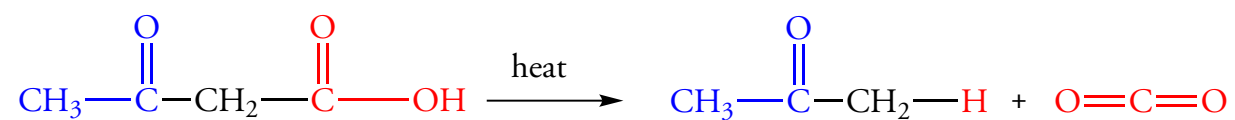
### Reduction with Diborane



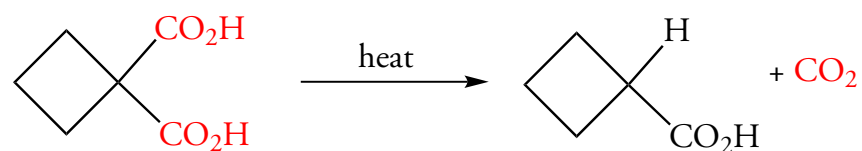
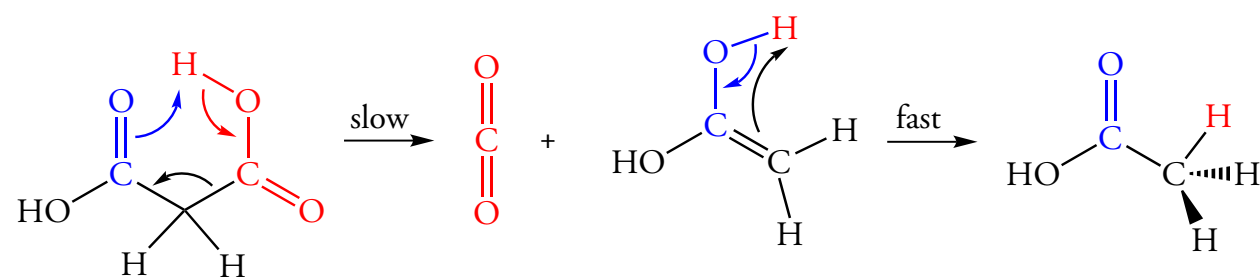
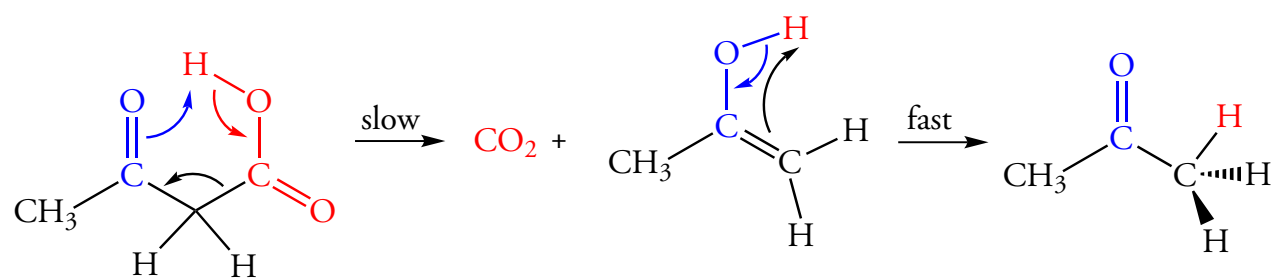
## 20.8 DECARBOXYLATION REACTIONS



malonic acid

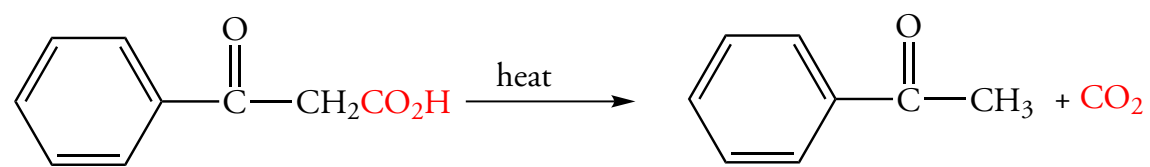


acetoacetic acid



1,1-cyclobutanedicarboxylic acid

cyclobutanecarboxylic acid

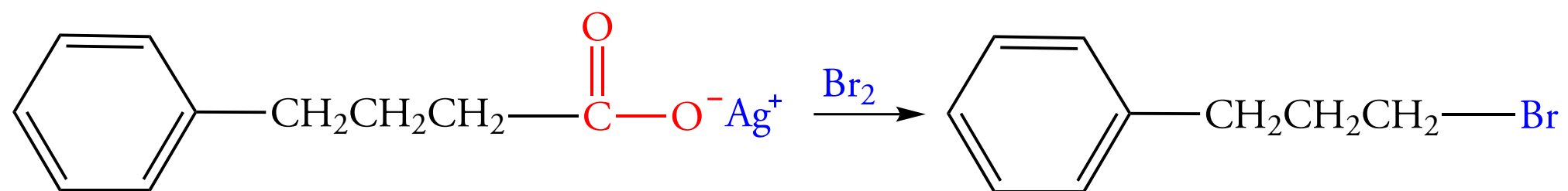


3-phenyl-3-oxopropanoic acid

1-phenyl-ethanone

## 20.8 DECARBOXYLATION REACTIONS

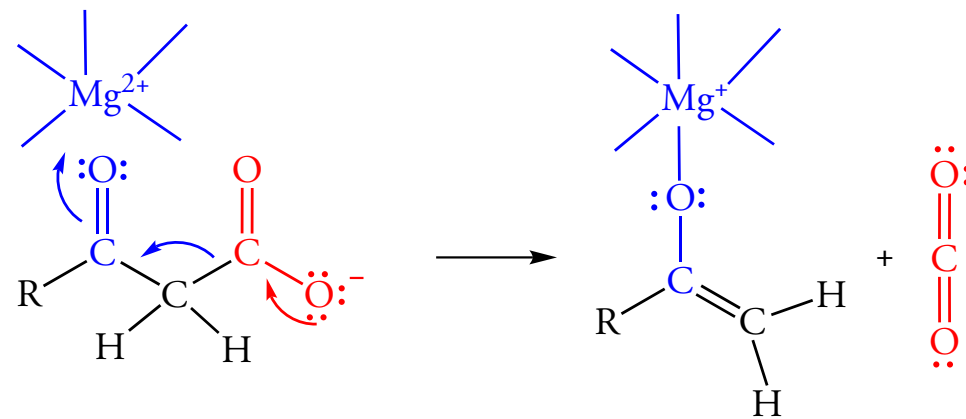
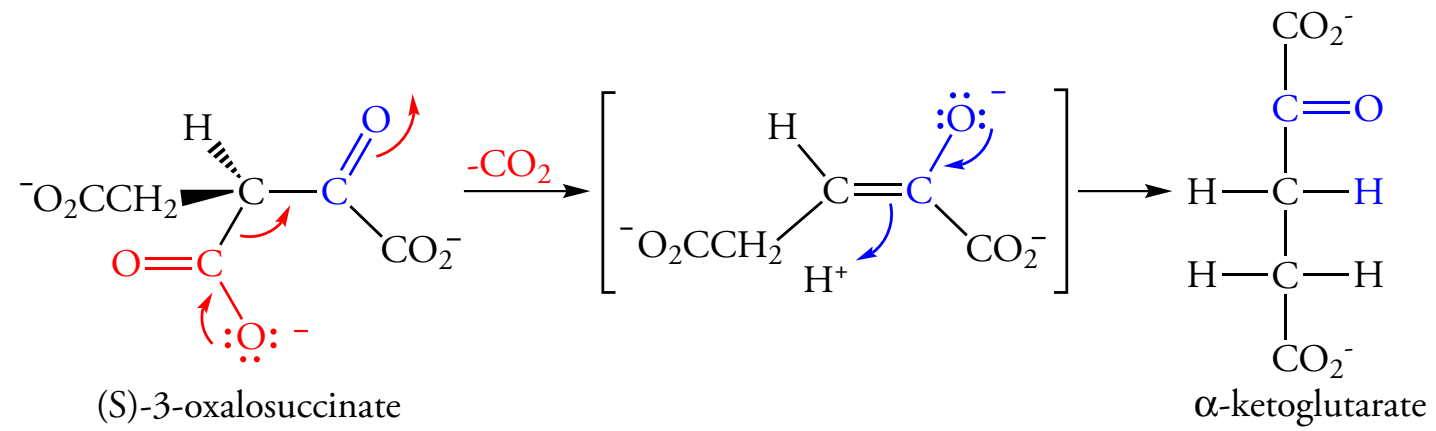
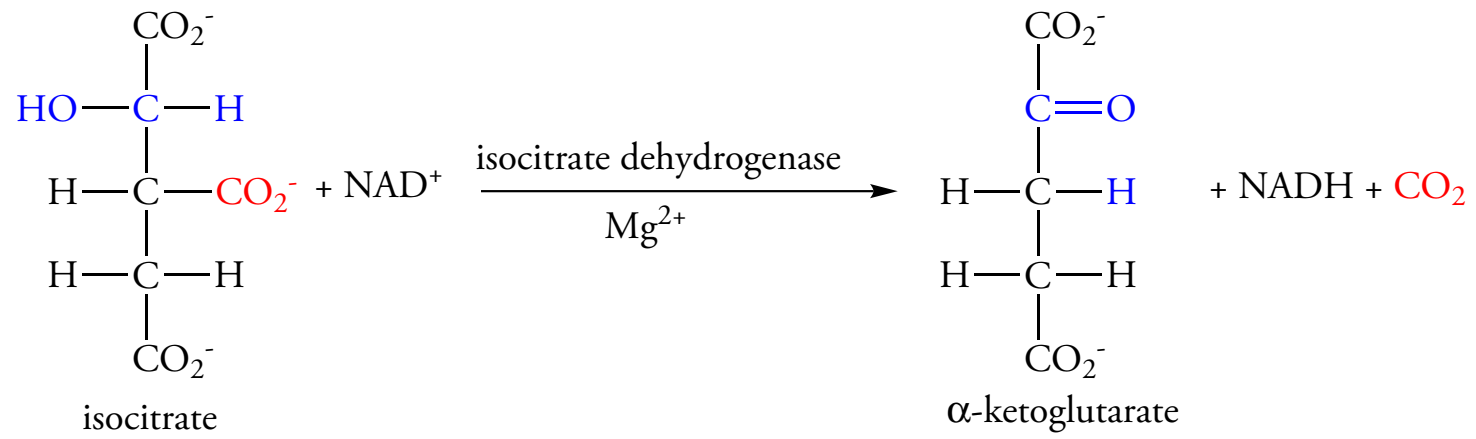
### The Hunsdiecker Reaction





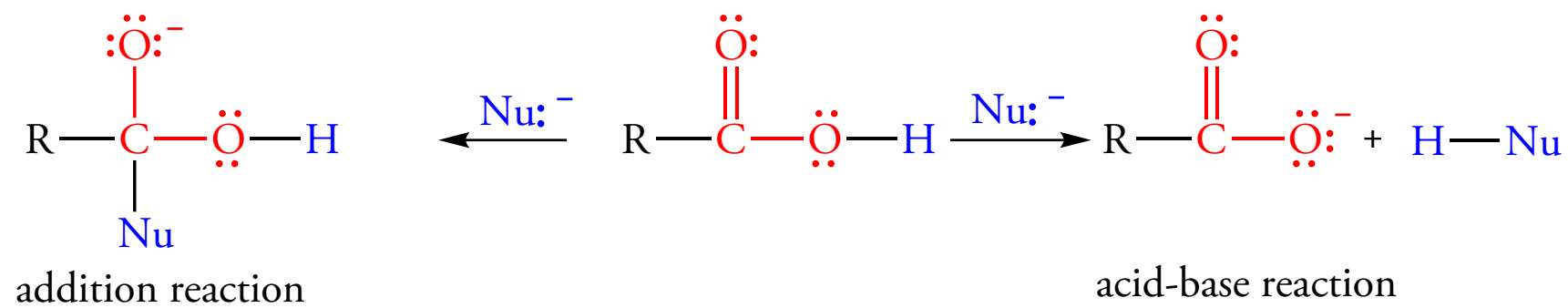
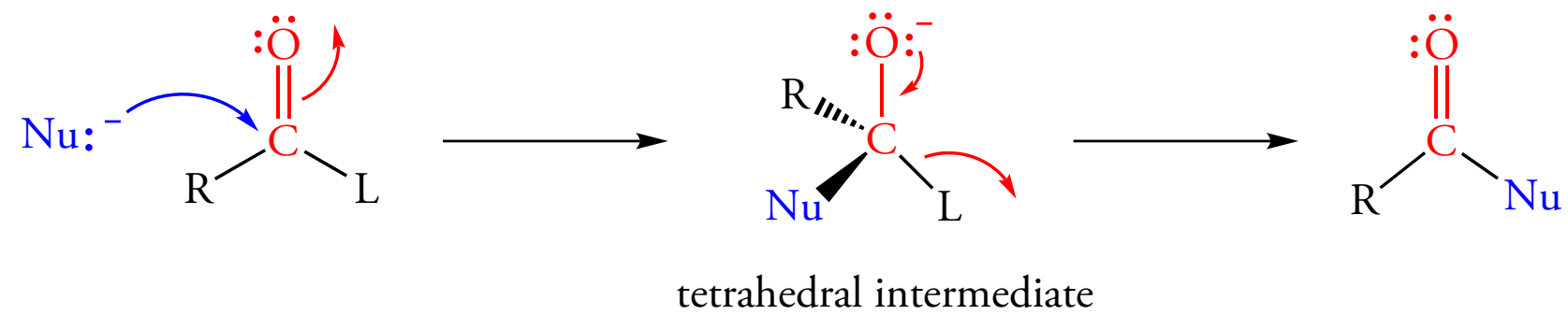
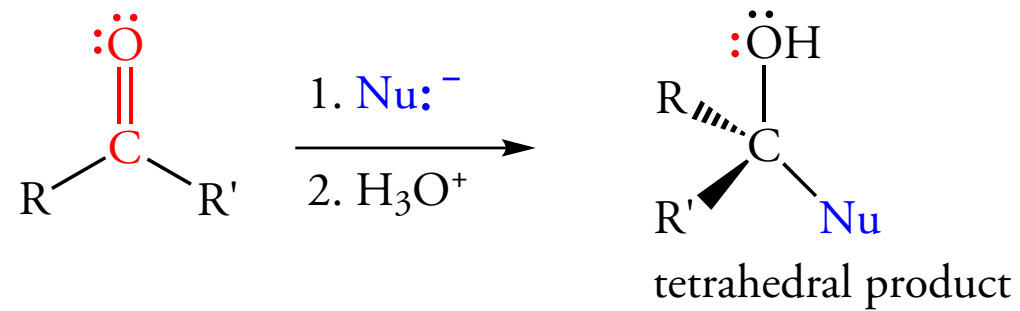
# 20.8 DECARBOXYLATION REACTIONS

## Biochemical Decarboxylation Reactions

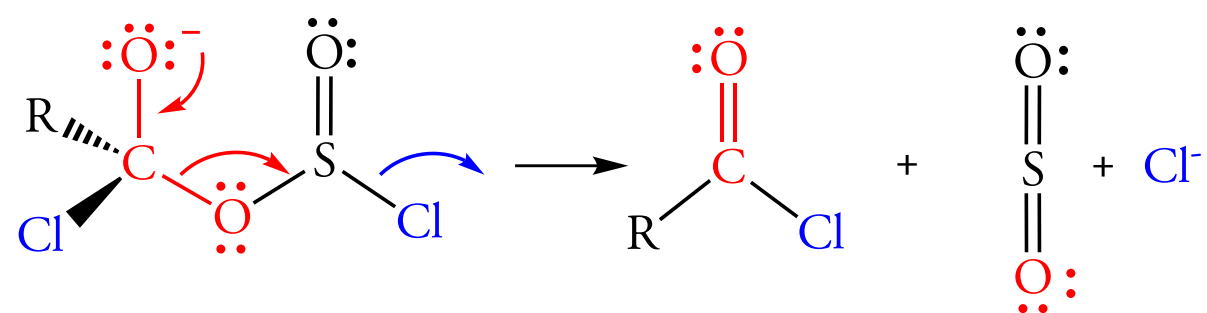
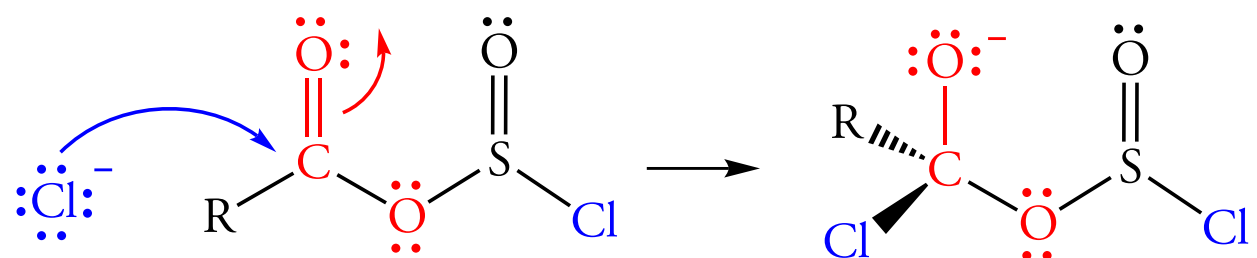
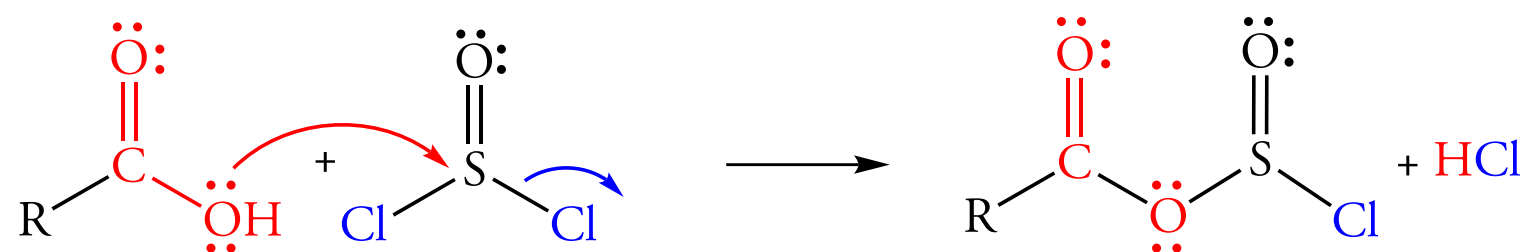
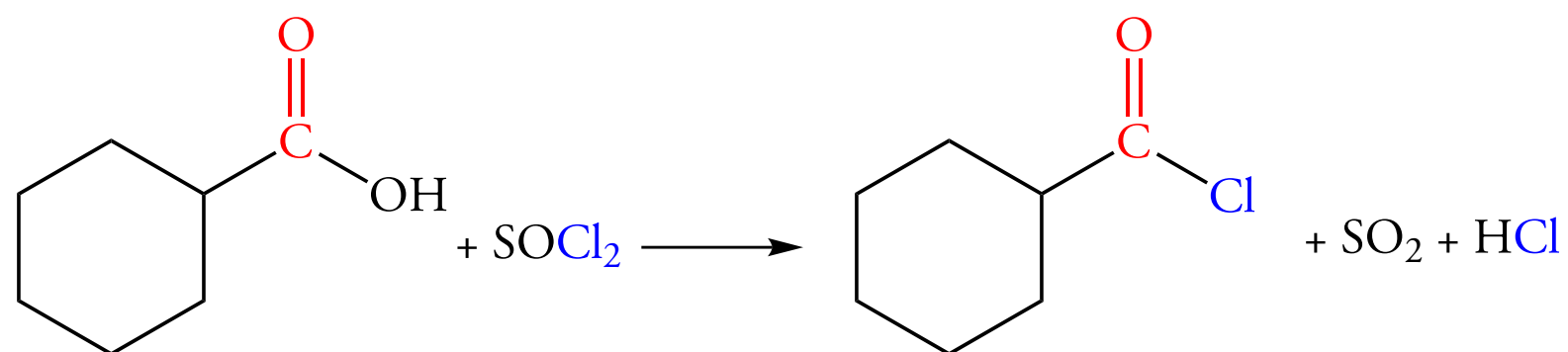


# 20.9 REACTIONS OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES: A PREVIEW

## Nucleophilic Acyl Substitution

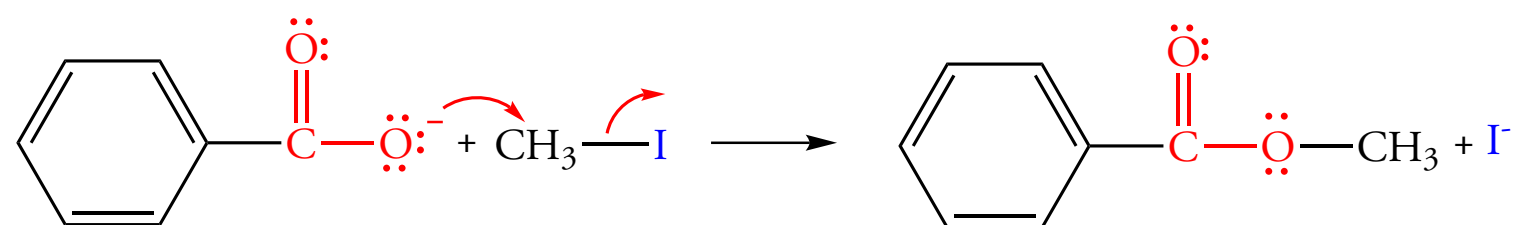


## 20.10 CONVERSION OF CARBOXYLIC ACIDS INTO ACYL HALIDES



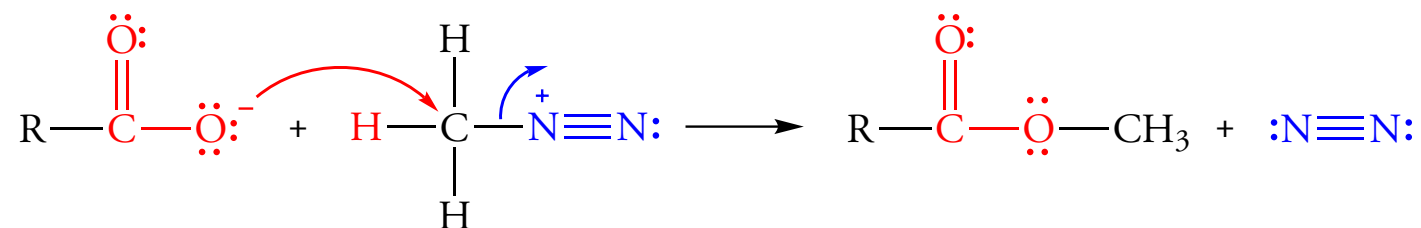
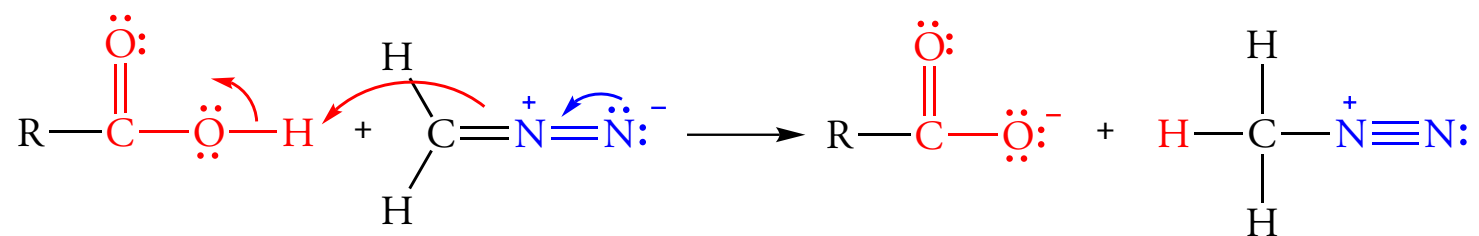
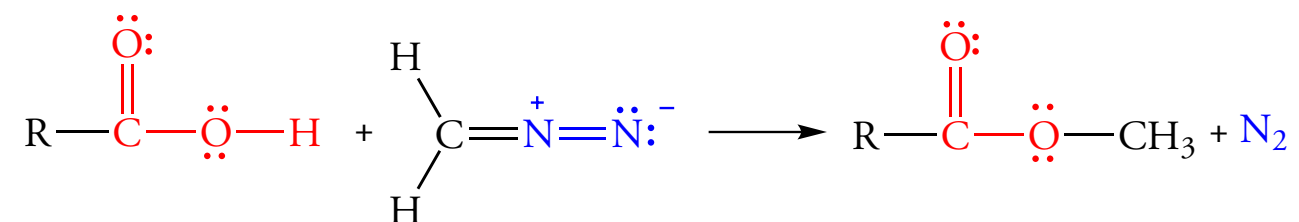
## 20.11 CONVERSION OF CARBOXYLIC ACIDS INTO ESTERS

### Alkylation of Carboxylate Anions



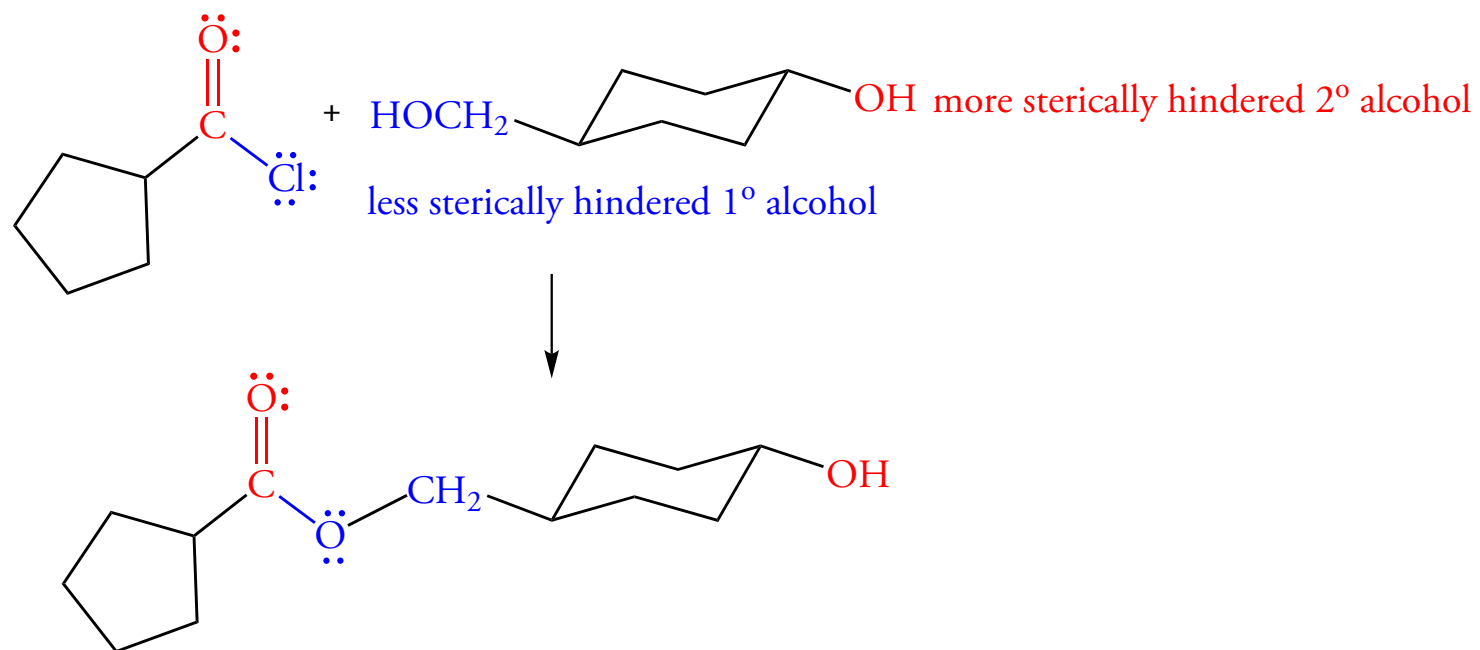
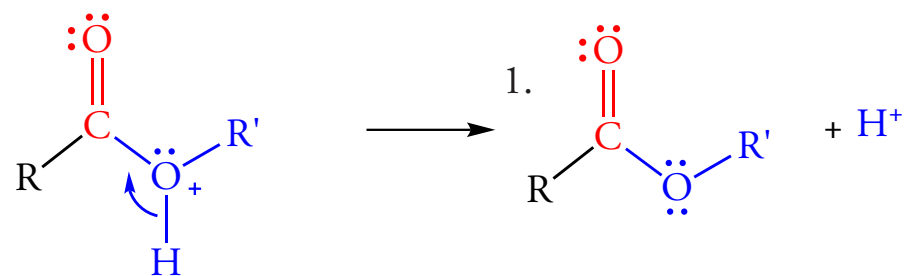
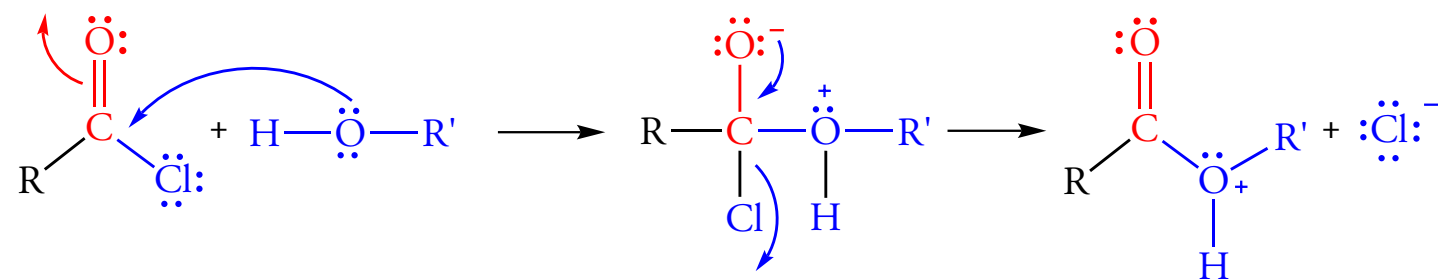
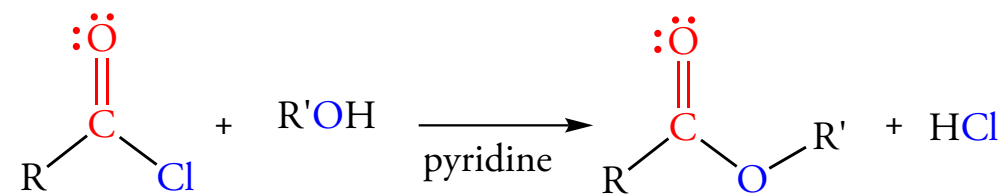
## 20.11 CONVERSION OF CARBOXYLIC ACIDS INTO ESTERS

### Esterification With Diazomethane



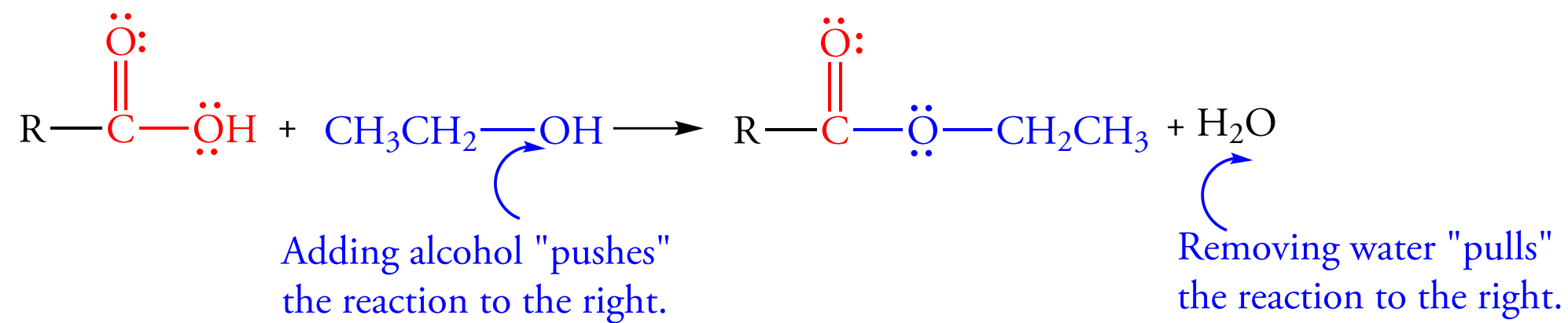
## 20.11 CONVERSION OF CARBOXYLIC ACIDS INTO ESTERS

### Reaction of Acyl Chlorides With Alcohols

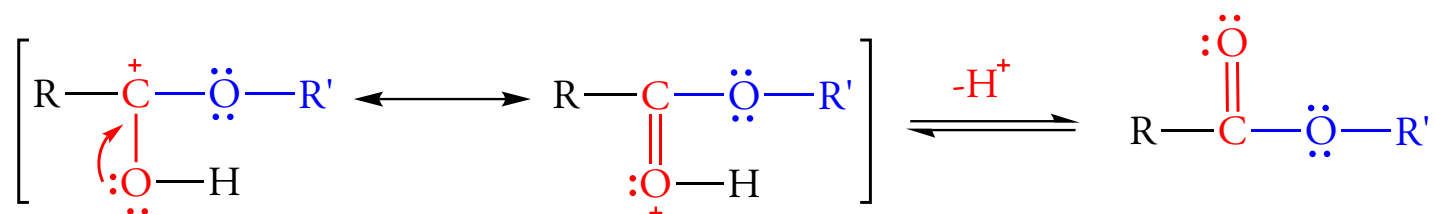
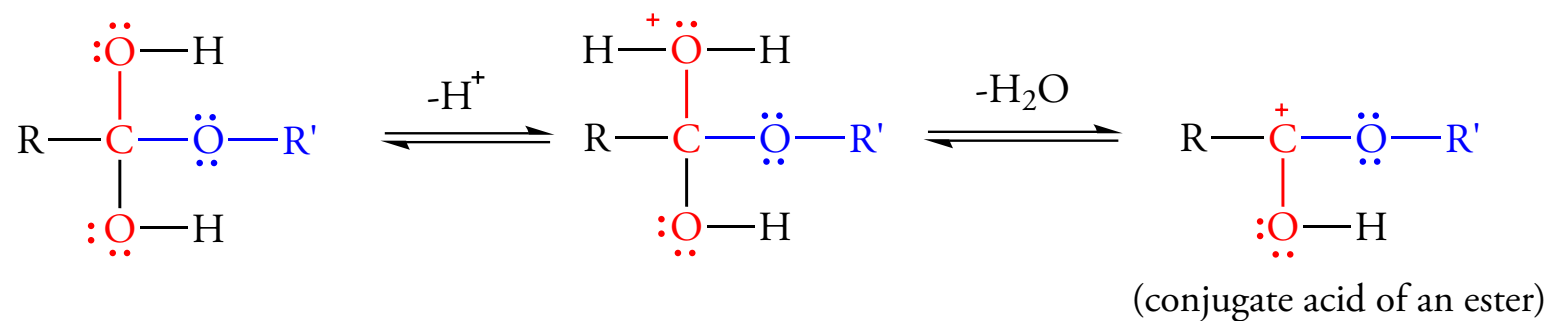
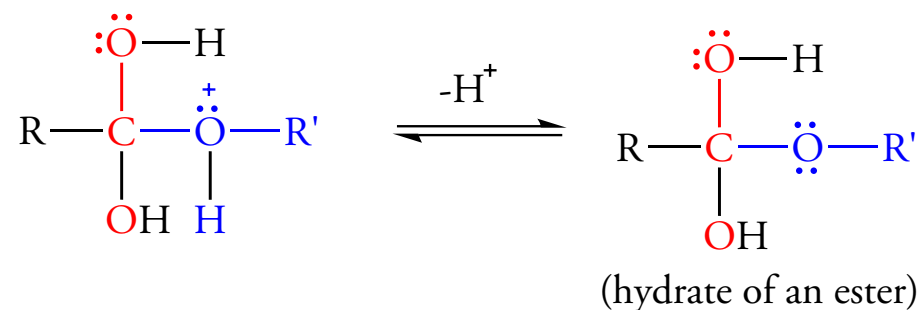
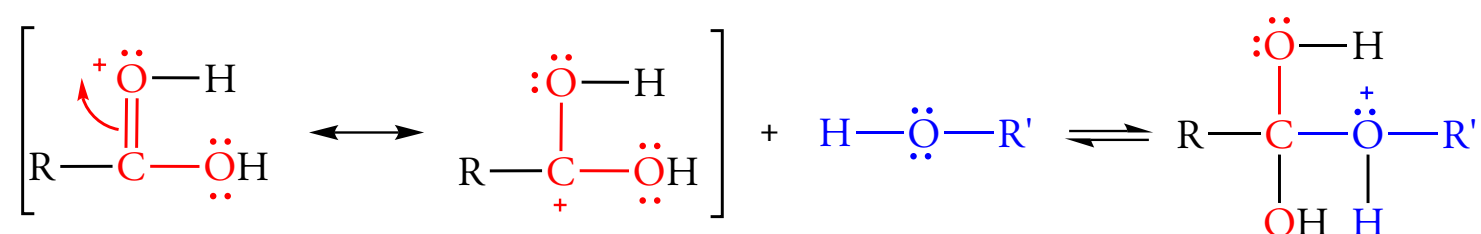
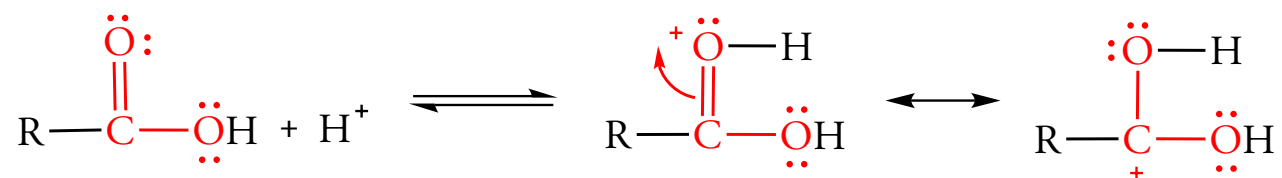
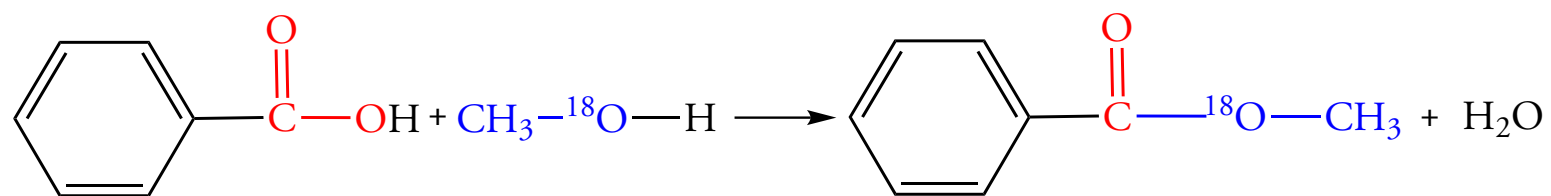


## 20.11 CONVERSION OF CARBOXYLIC ACIDS INTO ESTERS

### Fischer Esterification



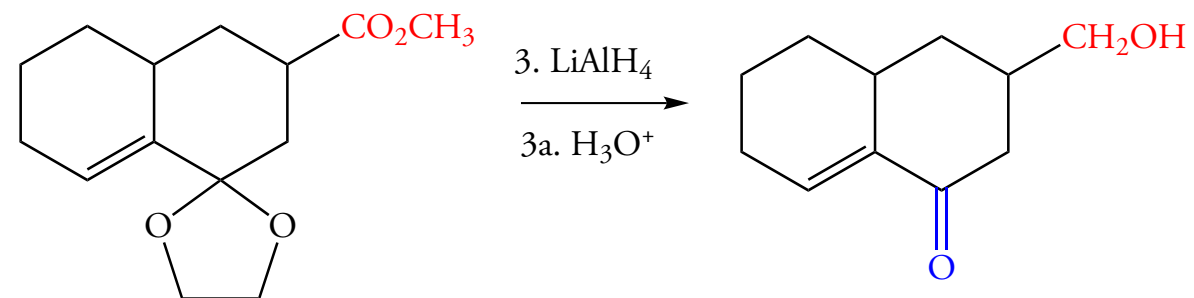
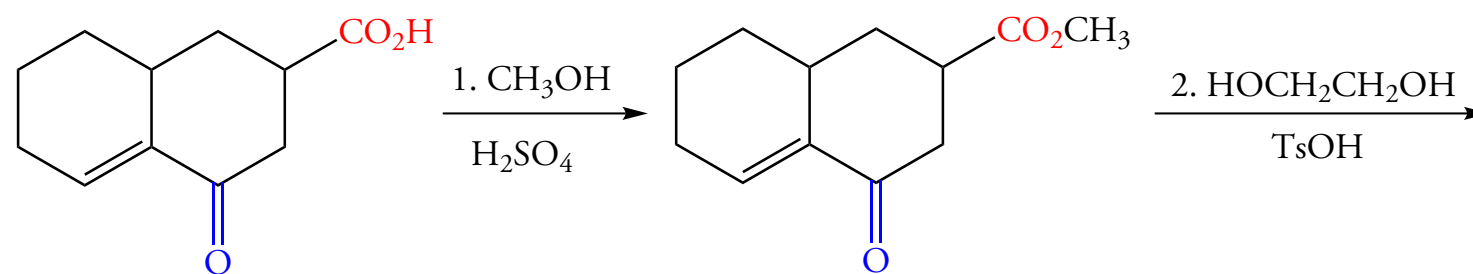
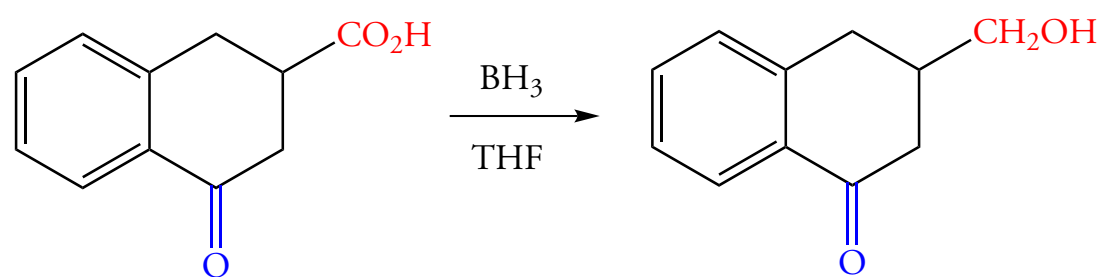
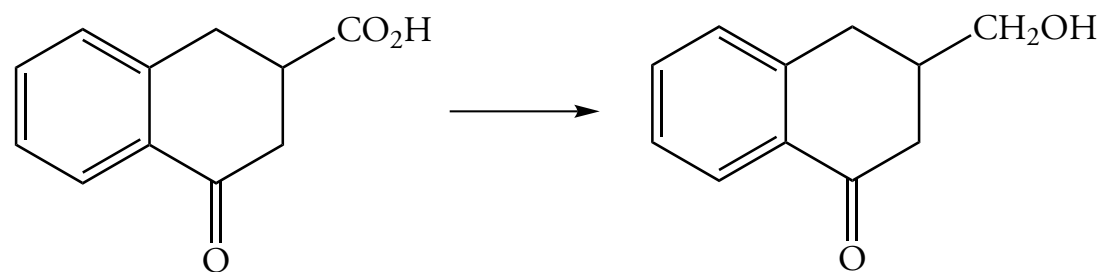
## 20.12 MECHANISM OF ESTERIFICATION





## 20.13 BRIEF SYNTHETIC REVIEW

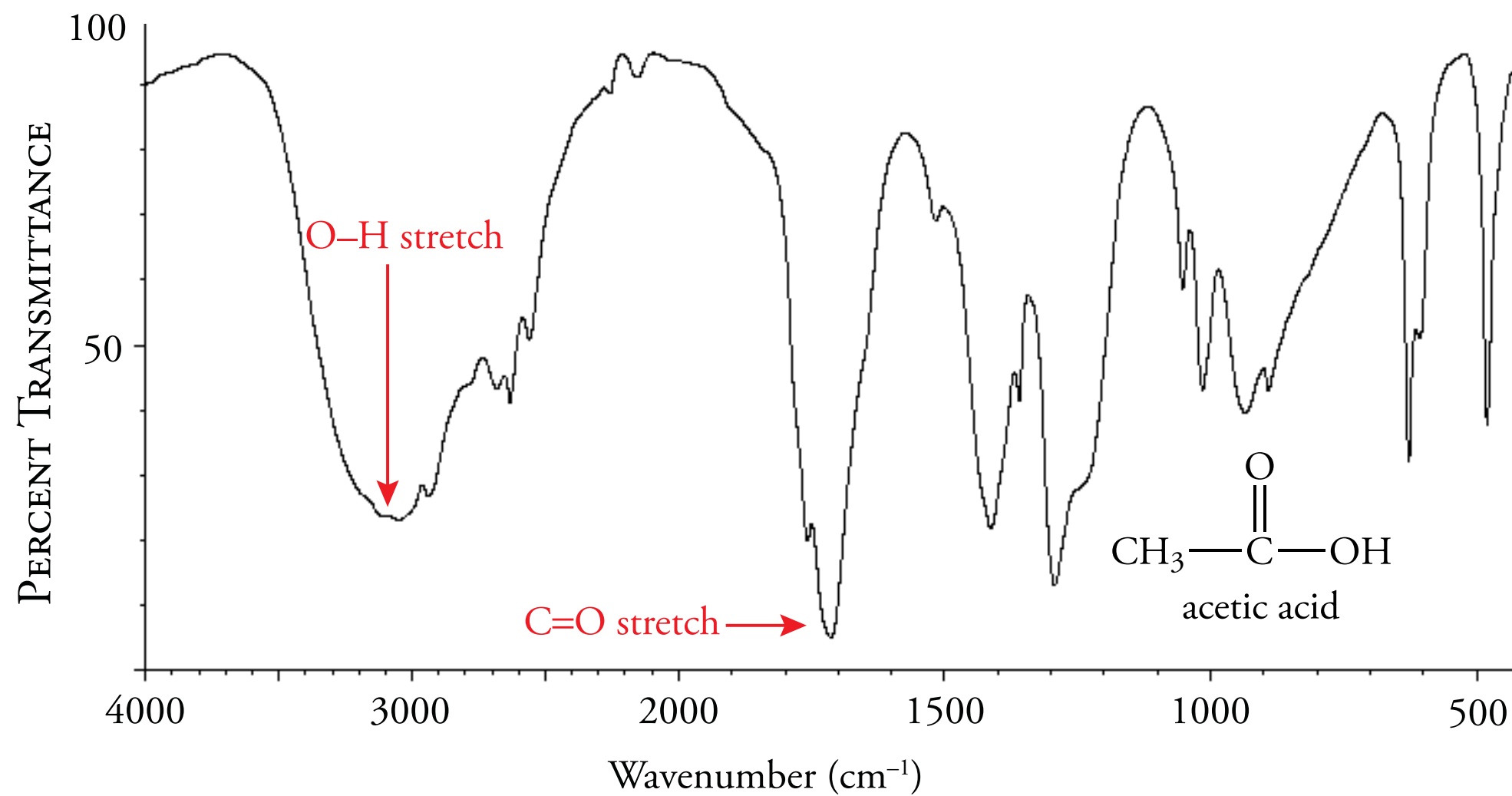
### Functional Group Modifications in Organic Synthesis



# 20.14 SPECTROSCOPY OF CARBOXYLIC ACIDS

## Infrared Spectroscopy

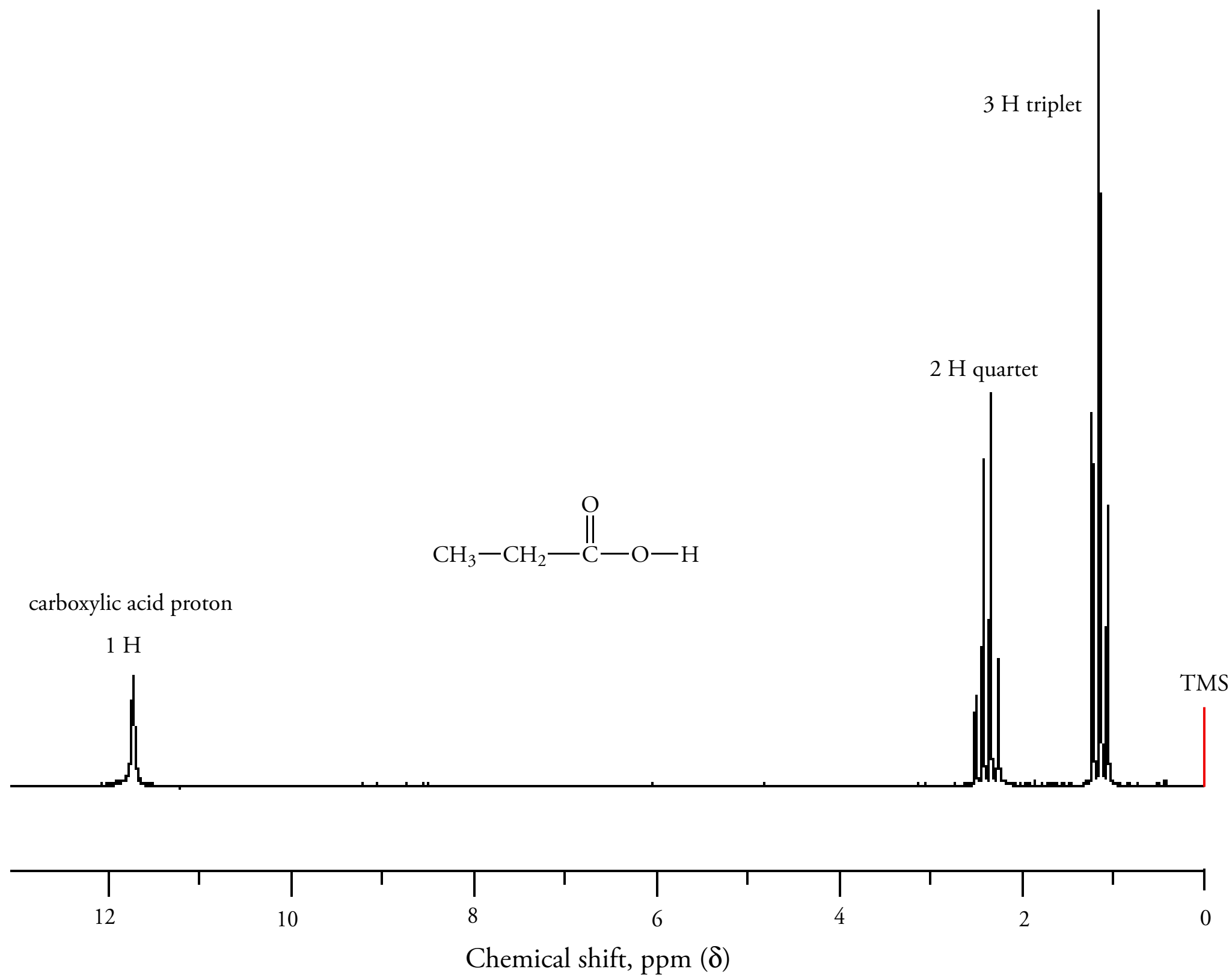
Figure 20.2 Infrared Spectrum of Acetic Acid



# 20.14 SPECTROSCOPY OF CARBOXYLIC ACIDS

## Proton NMR Spectroscopy

Figure 20.3 Proton NMR Spectrum of Propanoic Acid



## 20.14 SPECTROSCOPY OF CARBOXYLIC ACIDS

### Proton NMR Spectroscopy

Figure 20.4 C-13 NMR Spectrum of Propanoic Acid

