

Carboxylic Acids & Derivatives

February 19, 2020

- A brief nod towards nomenclature & properties.
- pKa review.
- Preparation of carboxylic acids: is anything new?
- The general addition-elimination mechanism and factors influencing reactivity.

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O'Leary office hours: T/Th 9:30-10:00 am, SN 208.

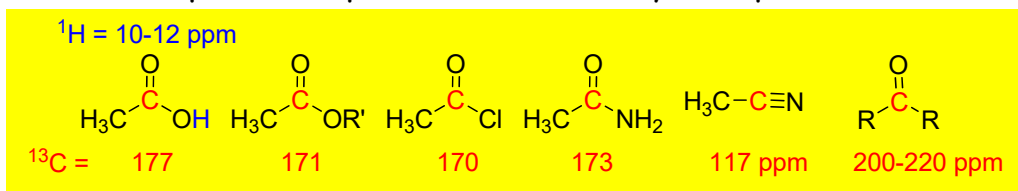
O'Leary's evening review session: Wednesdays 7:00 PM, SN Aud. **Course website:** <http://pages.pomona.edu/~djo04747/110/>

Suggested Problems for Exam 2. 10e: 16.20, 24, 30, 33, 35, 41, 44, 45, 47. 11e: 16.23, 27, 33, 36, 38, 44, 47, 48, 50. 10e/11e: 17.20, 17.28, 17.31, 17.33, 17.35, 17.38, 17.41, 17.42, 17.47.

Carboxylic and Dicarboxylic Acids

Structure	Systematic	Common	mp (°C)	bp (°C)	H ₂ O sol (g/100ml)	pK ₁	pK ₂
HCOOH	methanoic	formic			∞	3.75	
CH ₃ COOH	ethanoic	acetic	16.6	118	∞	4.76	
CH ₃ CH ₂ COOH	propanoic	propionic			∞	4.87	
CH ₃ CH ₂ CH ₂ COOH	butanoic	butyric			∞	4.81	
CH ₃ (CH ₂) ₃ COOH	pentanoic	valeric			5	4.82	
CH ₃ (CH ₂) ₄ COOH	hexanoic	caproic			1	4.84	
CH ₃ (CH ₂) ₁₀ COOH	dodecanoic	lauric			0.006	5.3	
CH ₃ (CH ₂) ₁₄ COOH	hexadecanoic	palmitic			.002	6.46	
CH ₃ (CH ₂) ₁₆ COOH	octadecanoic	stearic			.0003	-	
Ph-COOH	benzoic	benzoic			0.34	4.19	
HO ₂ CCO ₂ H		oxalic				1.2	4.2
HO ₂ CCH ₂ CO ₂ H		malonic				2.9	5.7
HO ₂ C(CH ₂) ₂ CO ₂ H		succinic				4.2	5.6
HO ₂ C(CH ₂) ₃ CO ₂ H		glutaric				4.3	5.4
HO ₂ C(CH ₂) ₄ CO ₂ H		adipic				4.4	5.6
HOOC  COOH		maleic				1.9	6.1
HOOC  COOH		fumaric				3.0	4.4

Spectroscopic Markers for Acyl Compounds

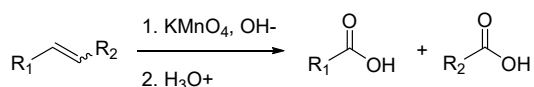


Functional Group	Approximate Frequency Range (cm^{-1})	1840	1820	1800	1780	1760	1740	1720	1700	1680	1660	1640	1620	1600
Acid chloride	1815–1785 1800–1770 (conj.)													
Acid anhydride	1820–1750 1775–1720 (conj.)													
Ester/lactone	1750–1735 1730–1715 (conj.)													
Carboxylic acid	~1760 or 1720–1705 1710–1680 (conj.)													
Aldehyde	1740–1720 1710–1685 (conj.)													
Ketone	1720–1710 1685–1665 (conj.)													
Amide/lactam	1650–1640													
Carboxylate salt	1650–1550													

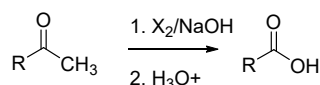
*Orange bars represent absorption ranges for conjugated species.

Preparation of Carboxylic Acids - A Beginning List

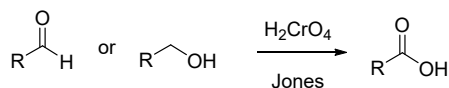
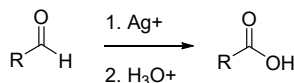
1. Oxidation of alkenes:



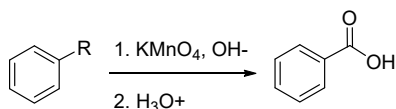
4. Oxidation of methyl ketones:



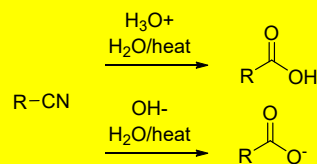
2. Oxidation of aldehydes & primary alcohols:



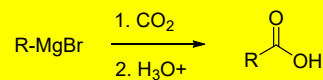
3. Oxidation (PacMan) of alkylbenzenes:



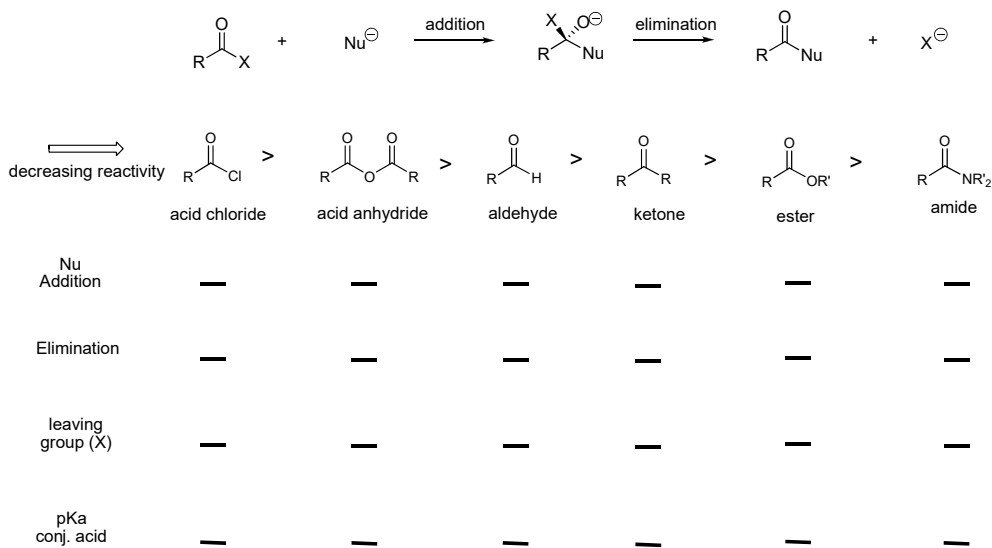
5. Hydrolysis of nitriles:



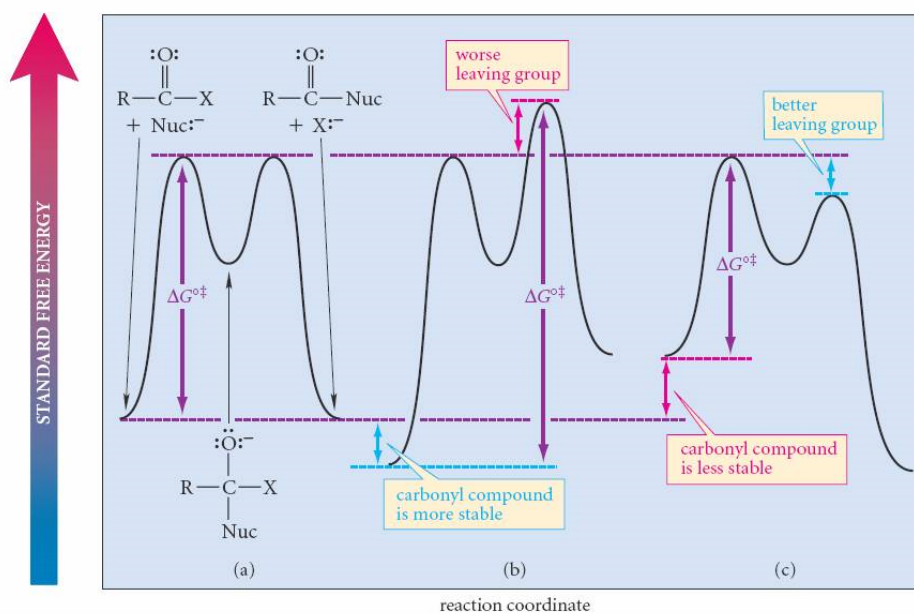
6. Carbonation of a Grignard:



Reactivity Order of Carbonyl Groups: General *Addition-Elimination Mechanism



*Effect of acid activation and/or proton transfers not shown.





A MECHANISM FOR THE REACTION

Basic Hydrolysis of a Nitrile

