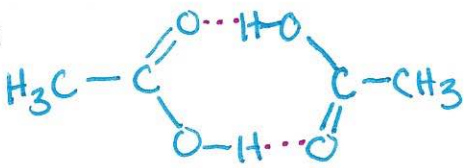
Carboxylic acids are very similar to ketones and alcohols in some respects...

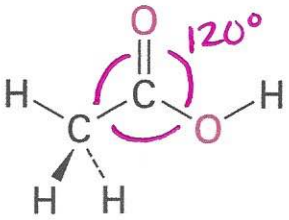
* acetic acid dimer



Chapter 20: Carboxylic Acids & Nitriles

Structure and Properties of Carboxylic Acids

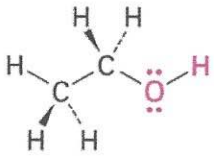
Like ketones, the carboxyl carbon is sp2 hybridized. A carboxylic acid group is therefore planar with 120° bond angles.



Like alcohols, carboxylic acids can participate in hydrogen bonding therefore, most carboxylic acids exist as cyclic dimers* held together by two hydrogen bonds. The strong hydrogen bonding has a noticeable effect on boiling points. Carboxylic acids boil far less easily than their corresponding alcohols

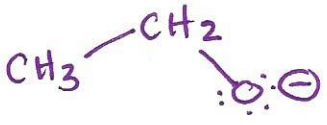
*Carboxylic acids are also more acidic than alcohols

Dissociation *Alcohols dissociate to give an alkoxide ion



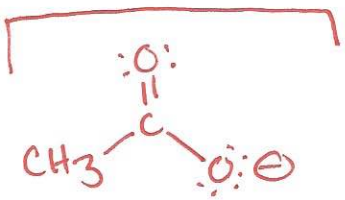
Ethanol

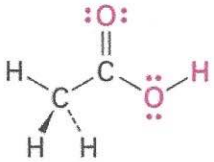
BP = ~78°C



ethoxide ion (localized charge on one oxygen)

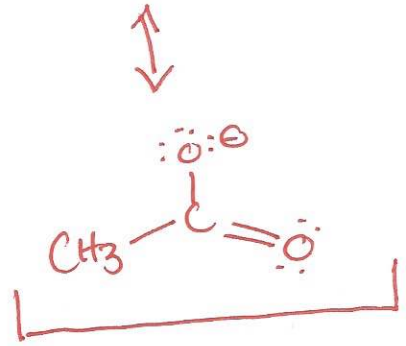
* higher in energy





Acetic acid

BP = ~118°C

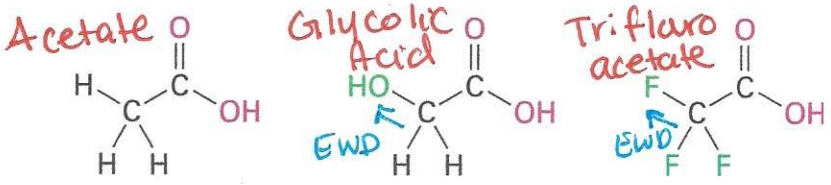


acetate ion (delocalized charge over two equivalent oxygen atoms)

* lower in energy

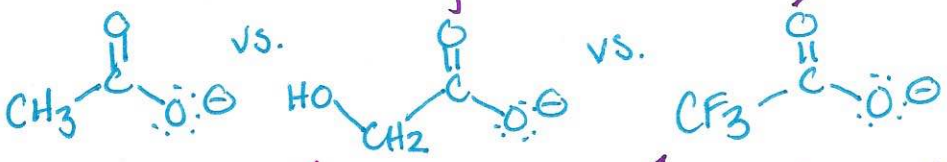
*Carboxylic acids dissociate to give acetate ion w/ resonance hybrid

Substituent Effects on Acidity



$pK_a = 4.76$ $pK_a = 3.83$ $pK_a = -0.23$

Acidity →



↑ OH, more EWD than CH_3 but less EWD than CF_3

↑ 3 electron withdrawing atoms will delocalize the negative charge ⇒ Therefore stabilize the ion and increase acidity

* The more stable the ion, the more acidic the molecule

* any factor that stabilizes the carboxylate anion will increase dissociation and therefore increase acidity

4-Chlorobutanoic acid

$pK_a = 4.52$

3-Chlorobutanoic acid

$pK_a = 4.05$

2-Chlorobutanoic acid

$pK_a = 2.86$

Acidity →

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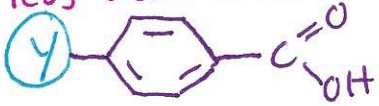
ED = electron donating

EWD = electron withdrawing

The effect of halogen substitution decreases as the substituent moves farther from the carboxyl. ⇒ Inductive effects = work through sigma bonds & are dependent on distance

* substituents on an aromatic ring strongly affect reactivity & stabilization. Aromatic rings w/ ED groups are less acidic then those w/ EWD groups

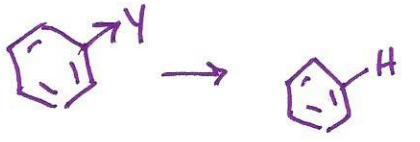


(E-D)

* CH_3O- methoxy decreases acidity by destabilizing the carboxylate anion

(E-WD)

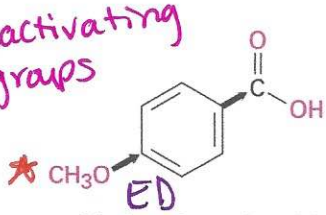
* NO_2 nitro groups increase acidity by stabilizing



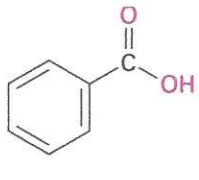
	Y	$K_a \times 10^{-5}$	pK_a
Stronger acid	$-NO_2$	39	3.41
	$-CN$	28	3.55
	$-CHO$	18	3.75
	$-Br$	11	3.96
	$-Cl$	10	4.0
	$-H$	6.46	4.19
	$-CH_3$	4.3	4.34
	$-OCH_3$	3.5	4.46
Weaker acid	$-OH$	3.3	4.48

deactivating groups

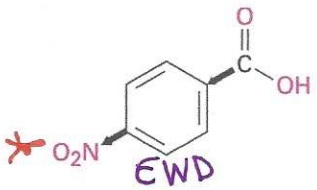
activating groups



p-Methoxybenzoic acid ($pK_a = 4.46$)



Benzoic acid ($pK_a = 4.19$)



p-Nitrobenzoic acid ($pK_a = 3.41$)

Acidity →

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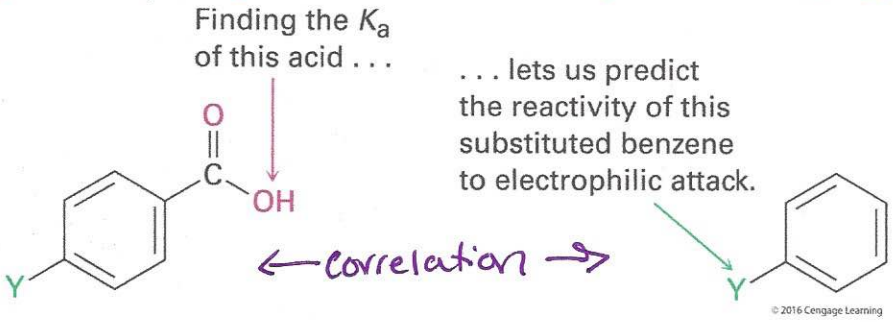
← Nitro groups are electron withdrawing

* It is much easier to measure the acidity of a substituted benzoic acid than it is to determine the reactivity of the aromatic ring so the correlation between the two is useful in predicting reactivity.

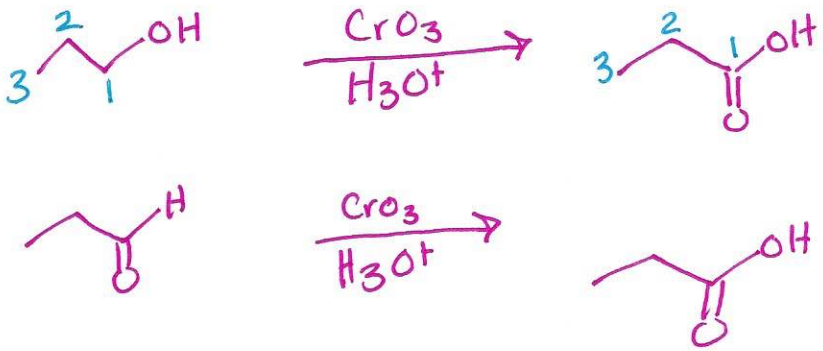


* If we want to know the effect of a certain substituent on electrophilic reactivity = find the acidity

Preparation of Carboxylic Acids

Review of reaction we already know:

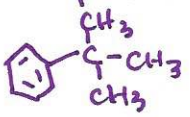
1. oxidation of primary alcohol or aldehyde

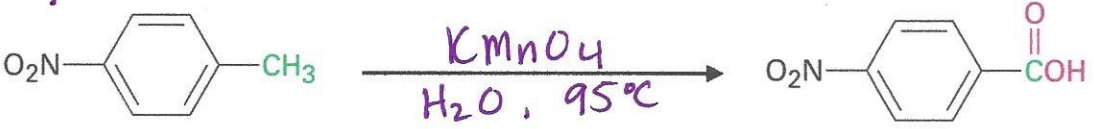


Note: $-COOH = -\overset{O}{\overset{\|}{C}}-OH$

2. Oxidation of a substituted alkyl benzene with $KMnO_4$ & $Na_2Cr_2O_7$

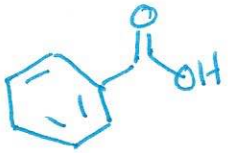
* 1° and 2° groups can be oxidized
* 3° groups are not affected →





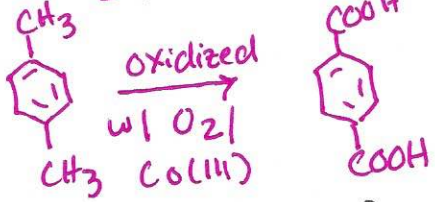
(alkyl benzene) butylbenzene

$KMnO_4$, H_2O, 95°C

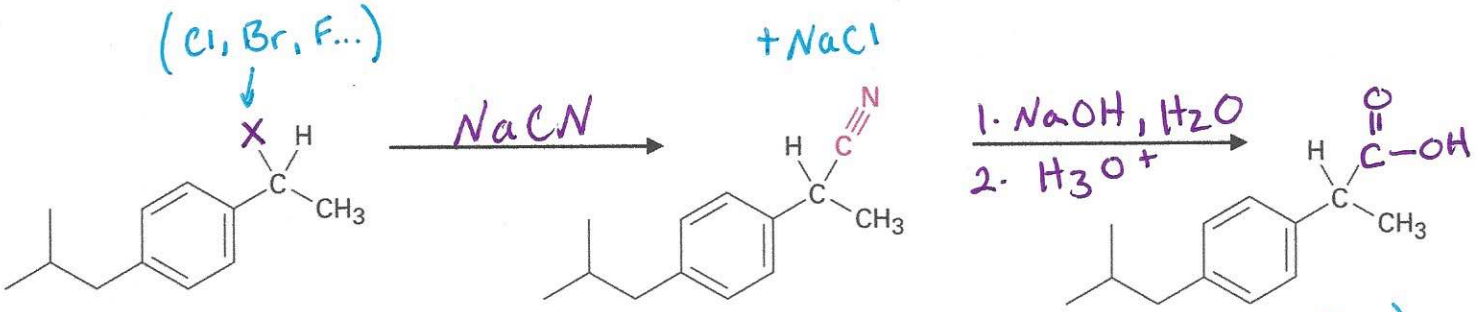


Benzoic acid

Polyester Fibers



3. Hydrolysis of Nitriles = S_N2, substitution

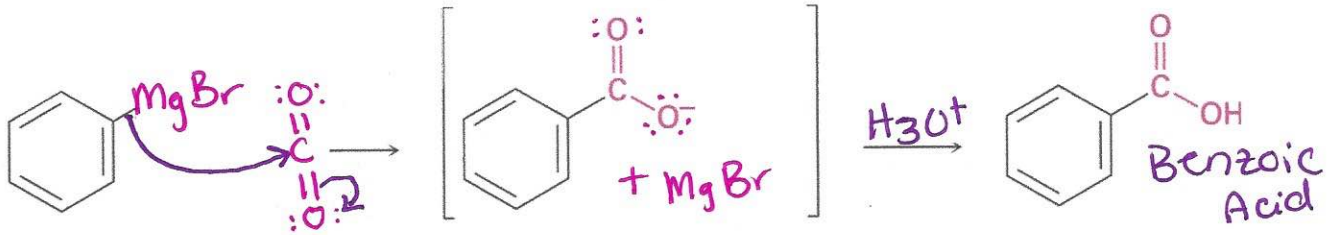


(Ibuprofen)

* Requires a 1° or 2° alkyl halide because it is a S_N2 reaction

4. Carboxylation of Grignard Reagents

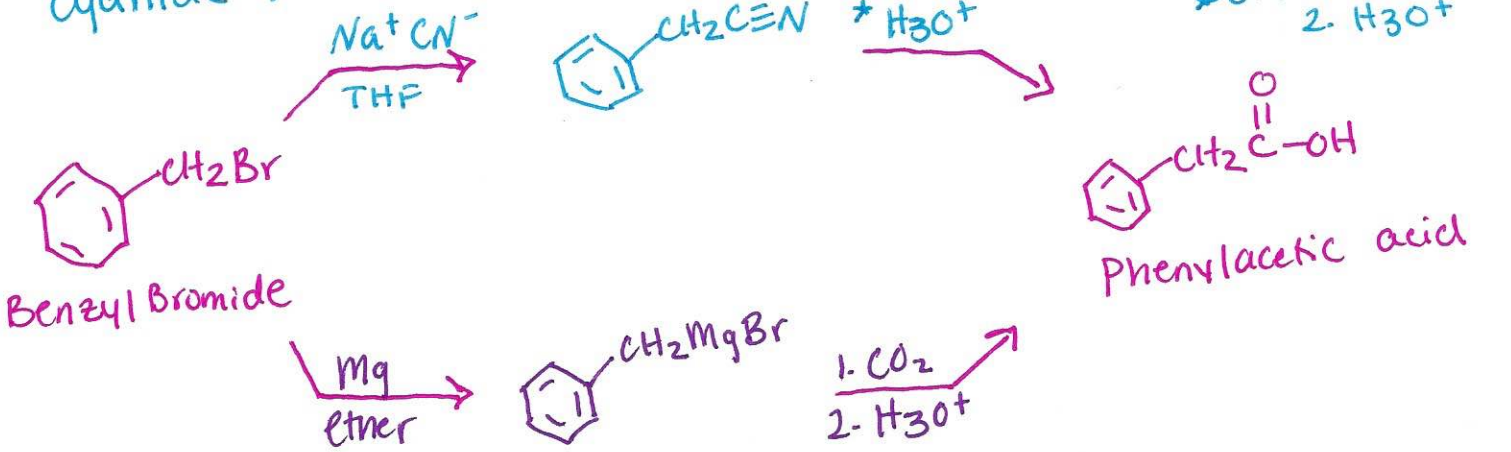
Grignard + CO_2 → metal carboxylate followed by protonation to yield carboxylic acid



magnesium halide adds to the C=O bond of carbon dioxide (nucleophilic addition) Then protonation of the carboxylate ion yields a free carboxylic acid.

How would you prepare phenylacetic acid ($PhCH_2CO_2H$) from benzyl bromide ($PhCH_2Br$)? * Two ways!

① S_N2 (so limited to 1° & 2° halides)
Cyanide ion displacement followed by hydrolysis



② Formation of Grignard reagent, followed by carboxylation. Limited to organic halides w/ out acidic hydrogens or reactive functional groups else where