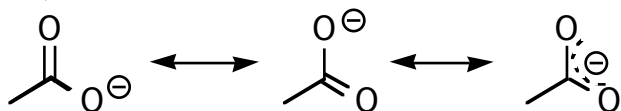


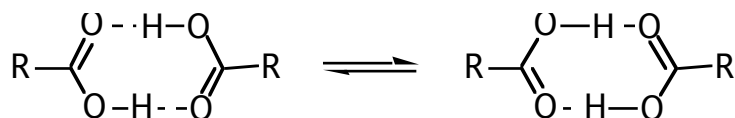
Carboxylic Acids

Carboxylic acids. You've seen them on the chalkboard a thousand times. But what does it all mean?

Carboxylic acids have one property that distinguishes them from most other organic compounds – they're acidic. Now not as acidic as fuming sulfuric acid, but still pretty darned acidic. The acidity of these compounds arises from the resonance stabilization of the conjugate base (bond lengths equalize):



Carboxylic acids undergo hydrogen bonding much like alcohols. However, in a carboxylic acid you have both a hydrogen bond donor *and* acceptor in the same molecule. These acids thus form highly stable dimers (as shown below). For small acids (e.g. acetic acid) this dimer cannot even be broken down by distillation – which explains why the boiling point for these acids is so high (the molecular weight is essentially doubled).



The acidity of these compounds can be modified by changing the substituents on the alkyl portion of the acid. Electron withdrawing groups make the molecule more acidic (by stabilizing the negative charge on the conjugate base), while electron-donating groups make it less acidic, by destabilizing that same charge. You should know this relationship already! It's the same one that determines good leaving groups and electrophiles, the stability of carbocations and carbanions, it is a major force in organic chemistry. Let me run this by you again:

Electron withdrawing groups stabilize negative charges

Electron donating groups *destabilize* negative charges.

'nuff said.

Protonation

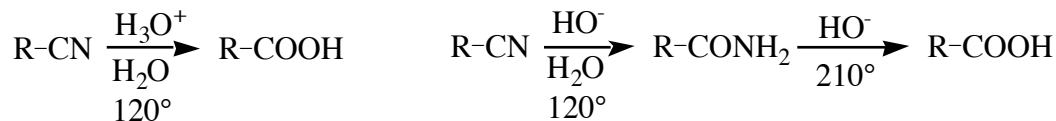
Preparation of carboxylic acids:

You've already seen a veritable plethora of methods for the preparation of carboxylic acids. Let me run a few by you just to make sure everyone is up-to-speed:

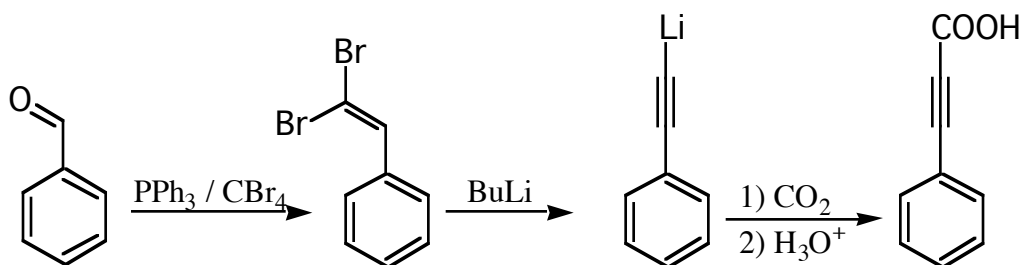
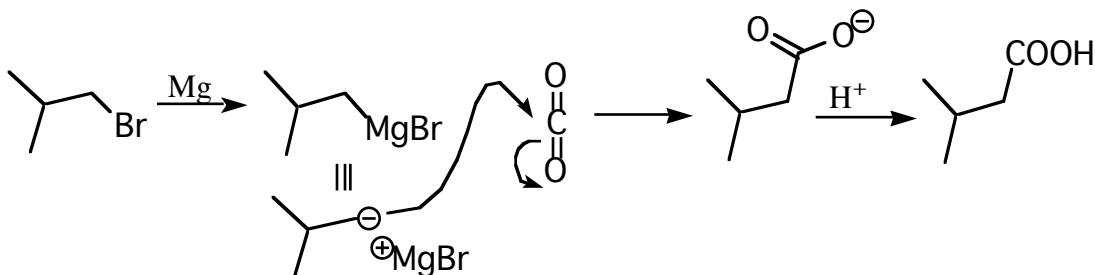
- 1) Oxidation of a PRIMARY alcohol with $\text{Na}_2\text{Cr}_2\text{O}_7$.
- 2) Oxidation of aromatic side chains containing benzylic hydrogens with KMnO_4
- 3) KMnO_4 oxidation of alkenes or alkynes (not common)
- 4) Oxidation of aldehydes with silver or hypochlorite.

There are a few other ways to get carboxylic acids out of various compounds. For example, nitriles (formed by the reaction of an alkyl halide with KCN) can be hydrolyzed under acidic (milder) or basic (very harsh) conditions to give the corresponding acid. If the nitrile is

hydrolyzed under basic conditions, the amide is the compound more commonly isolated (rather high temperatures are required to get the acid under basic conditions):



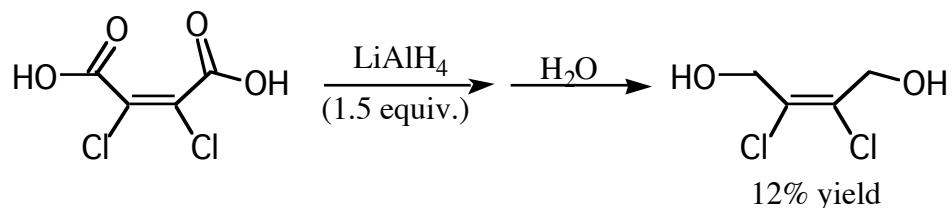
A somewhat more common method for the preparation of carboxylic acids is the carboxylation of Grignard reagents. This is really a straightforward reaction – a Grignard reagent is simply quenched with dry ice (solid CO_2). The Grignard attacks the carbonyl group to form the acid, which is relatively inert to further attack. In fact, any of the **R-M** reagents we've talked about in the past will do this carboxylation reaction:



Annihilation of carboxylic acids:

Just as carboxylic acids can be formed by the oxidation of primary alcohols, primary alcohols are formed by the reduction of carboxylic acids. There really are only two ways to do this reduction:

1) If the carboxylic acid is in conjugation with a double bond, then the only reagent that can be used is LiAlH_4 (Lithium Aluminum Hydride). The reaction is difficult - often requiring a fair amount of time and heat, and the yields are often low. But it is the only method that works!



For non-conjugated acids, there is a much more efficient reagent. A solution of borane (BH_3) in tetrahydrofuran (THF) very efficiently reduces acids to the corresponding primary alcohol:

