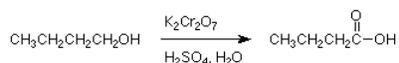


1.12: Carboxylic Acids

Oxidation of Primary Alcohols

There are two types of reactions which can make carboxylic acids. We will look first at those that depend upon oxidation of groups from a lower oxidation level (fewer oxygens, more hydrogens). Then we'll see that there are reactions which make a carbon carbon bond on the way to making a carboxylic acid.

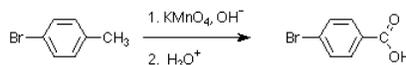
As you might suspect, carboxylic acids can be made by oxidizing groups which are less oxidized. The most important of these is the primary alcohol group. A typical reaction is:



We recognize the oxidizing agent, potassium dichromate, as the same reagent that was used in oxidizing aldehydes to carboxylic acids. Chromium is in oxidation level six in dichromates and it is reduced to oxidation level three in this process. The details of the reduction of chromate are complex, and we will not be concerned with them. The oxidation of aldehydes also produces carboxylic acids, but since aldehydes are less readily made than carboxylic acids, this process is not used much.

Oxidation of Side Chains on Aromatic Rings

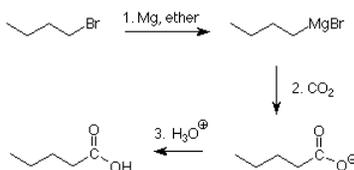
Another oxidative process seems at first not to involve a functional group. Alkyl groups (usually methyl groups) attached directly to an aromatic ring are also oxidized to carboxylic acids. Since the methyl group contains only sigma C-H bonds, it doesn't look like a likely place for reaction. It is influenced by the neighboring aromatic ring, though, so reaction does occur. This is somewhat like the special reactivity of the alpha C-H bonds of a ketone or aldehyde. Here's an example:



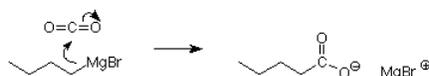
Remember, this reaction **requires** the presence of an aromatic ring next to the alkyl group which is to be oxidized. Any carbons beyond the first one are lost in this process, which is one of the few reactions which breaks a carbon-carbon bond.

Making a Carbon-Carbon Bond

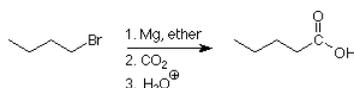
There are two reaction sequences which make carbon-carbon bonds on the way to carboxylic acids. The first is another use of the Grignard reagent. Remember that Grignard reagents react with carbonyl compounds to make alcohols. While we don't usually think of it that way, carbon dioxide is a carbonyl compound ($\text{O}=\text{C}=\text{O}$). If a Grignard reagent is used to deliver a nucleophilic carbon atom to the carbonyl carbon of the carbon dioxide, we get a carboxylic acid (after quenching with aqueous acid).



The attack of the Grignard reagent on the carbon dioxide is directly analogous to the same step in reactions of other carbonyl compounds:

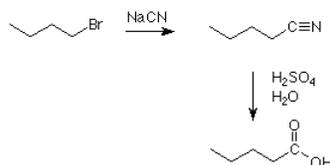


Here's the entire sequence presented in the more compact format we used for Grignard additions earlier:



Notice that the product has one more carbon than the bromoalkane we started with, and that this carbon is in a carboxylic acid group.

There is also another way to make a new carbon-bond and wind up with a carboxylic acid. If we have a primary alkyl halide (primary means that the carbon which is bonded to the halogen is bonded to only one other carbon atom, its other two bonds are to hydrogen), we can react it with sodium cyanide. The cyanide ion will replace the halogen, and this makes a new carbon-carbon bond. The product is called a nitrile. Its carbon-nitrogen triple bond can be hydrolyzed with aqueous acid to produce a carboxylic acid. The sequence is as follows (normally, the nitrile is isolated and then hydrolyzed in a separate reaction):

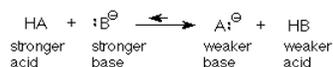


We won't look at the details of the mechanisms of either of these reactions now. You might usefully speculate about the hydrolysis of the nitrile. You could begin by thinking of the C-N triple bond as being like a carbonyl group. After all, it does include a pi bond between carbon and an electronegative atom, much like the pi bond in a carbonyl group.

Acid and Base Strengths

The remaining issue with carboxylic acids is to understand why they are acidic. We can experience their acidity by tasting vinegar - which is a dilute solution of acetic acid in water. The Lowry-Bronsted model of acids is useful for this. Let's refresh our memories on this model and on the interpretation of the term pK_a .

When we think about acids using the Lowry-Bronsted model, we think of a molecule which can donate a proton (H^+). A base is a molecule which can accept a proton (using the pair of electrons which are the defining feature of a Lewis base). Stronger acids donate protons readily to stronger bases. The products of this transaction are weaker acids and weaker bases. Here's the pattern.



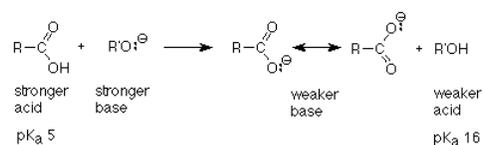
Notice particularly that a strong acid is strong because it readily donates a proton. That means that its conjugate base (the base which remains after the proton is gone) is weak. After all, if the base were strong, it would grab the proton back and the acid couldn't give it away. When we describe an acid as strong, by saying that it has a small pK_a , we are also saying that its conjugate base is weak. HCl is a strong acid ($\text{pK}_a \approx -7$). When we say that, we are also saying that Cl^- is a weak base. The conjugate base of an acid whose pK_a is small or negative is a weak base. This means that we can use a pK_a table like Table 2.1 on p 43 of Brown to keep track of both acidity (strong acids have small or negative pK_a 's) and basicity (weak bases come from strong acids with small or negative pK_a 's).

Carboxylic Acid Acidity - Carboxylate Ion Basicity

This also means that we can restate the question "Why are carboxylic acids acidic?" to say "Why are the conjugate bases of carboxylic acids such weak bases?" To put this into context, notice that carboxylic acids have pK_a 's of about 5, while water and alcohols have pK_a 's of about 16. What makes the conjugate base (we'll call it a carboxylate ion) of a carboxylic acid so weak compared to a hydroxide (OH^-) or alkoxide (RO^-) ion?

As usual, we'll try to find our explanations in structure. There is one obvious difference between a carboxylate ion and an alkoxide ion. The carboxylate ion has two electronegative oxygens to only one for the alkoxide ion. These electronegative atoms would hold the electron pairs more tightly, which means that the electron pairs would be less available to make a bond to a proton. Less available electron pairs means a weaker base.

That accounts for some of the weakness of carboxylate ions as bases, but there's also a more subtle feature. Notice that we can move electrons between pi-bonding and unshared pair situations without changing the structure of the carboxylate ion. We recognize this as resonance and we recognize that it will lower the energy of a carboxylate ion compared to that of an alkoxide ion in which such resonance is not possible. Lower energy means more stable, more easily formed and less reactive, all of which adds up to a weaker base. Consequently the conjugate carboxylic acid is stronger than one whose conjugate base doesn't have the resonance possibility.



The somewhat paradoxical outcome of this is that carboxylic acids are stronger acids than alcohols because carboxylate ions, their conjugate bases, are weaker bases than alkoxides. This is due in large part to resonance stabilization of the carboxylate ions, which cannot happen in alkoxides.

This understanding of the structure of carboxylate ions also helps us understand how it is that when a Grignard reagent reacts with carbon dioxide, only one of the two carbonyl groups reacts. The product of this reaction is a carboxylate ion. It is resonance stabilized so the "real" structure is about halfway between the two resonance structures. That means that each C-O bond is halfway between a single and a double bond -- a bond and a half. Such a bond would be much less reactive than the double bond of a carbonyl group, so it isn't surprising that the Grignard reagent reacts with carbon dioxide in preference to the carboxylate ion.

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