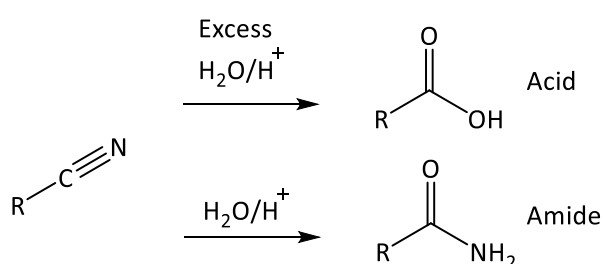


Carboxylic acids

- 1- Structure
- 2- Nomenclature of carboxylic acids
- 3- Physical properties
- 4- Synthesis of carboxylic acids

- **FROM NITRILES:**

The nitrile is heated under reflux with dilute hydrochloric acid. Instead of getting an ammonium salt as you would do if the reaction only involved water, you produce the free carboxylic acid.

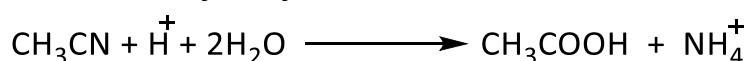


An alternative way to accomplish the same result is to treat the halide with potassium cyanide (KCN) or sodium cyanide (NaCN) and then hydrolyse the resulting nitrile, as mentioned above; e.g., $\text{RBr} + \text{KCN} \rightarrow \text{RCN} \rightarrow \text{RCOOH}$.

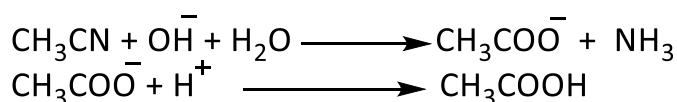
The two procedures are complementary. Although all nitriles can be hydrolysed to the corresponding acid and all Grignard reagents react with carbon dioxide, the halide reactions are more limited. Many types of halides (including aromatic halides) do not react with NaCN or KCN. On the other hand, while Grignard reagents can be made from many of the halides that do not react with NaCN or KCN (including aryl halides), they cannot be made from halides that contain certain other functional groups, such as alcohol, carboxylic ester, aldehyde, or ketone groups.

Two procedures of hydrolysis of nitriles are used to synthesise carboxylic acid but you must be careful to get this right.

1. **Acid hydrolysis**

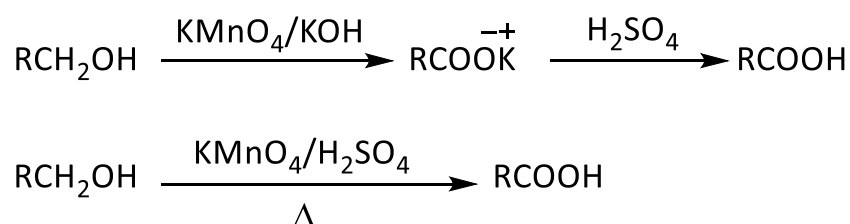


2. **Alkaline hydrolysis**



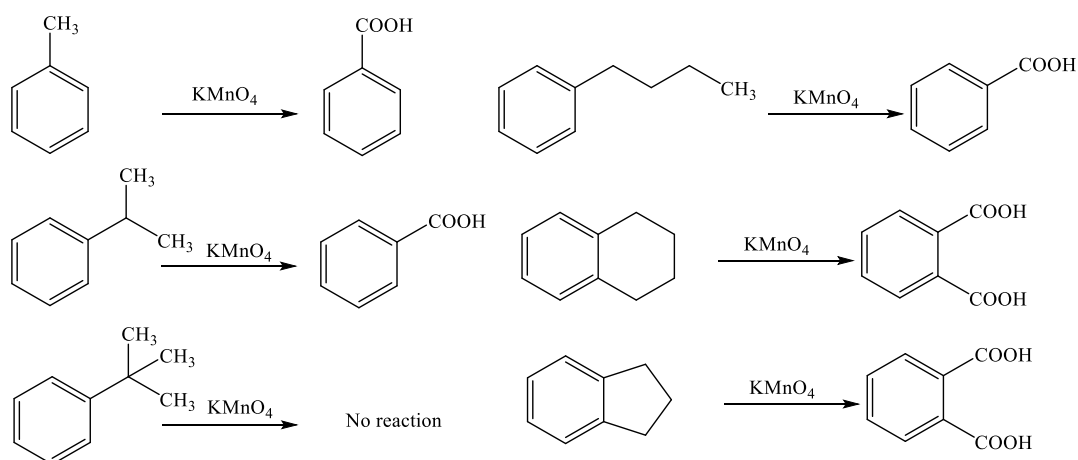
• **FROM PRIMARY ALCOHOLS (Oxidation):**

The oxidation of primary alcohols is a common method for the synthesis of carboxylic acids: $\text{RCH}_2\text{OH} \rightarrow \text{RCOOH}$. This requires a strong oxidizing agent, the most common oxidants: chromic acid (H_2CrO_4), potassium permanganate (KMnO_4), and nitric acid (HNO_3). Aldehydes are oxidised to carboxylic acids more easily (by many oxidizing agents), but this is not often useful, because the aldehydes are usually less available than the corresponding acids.



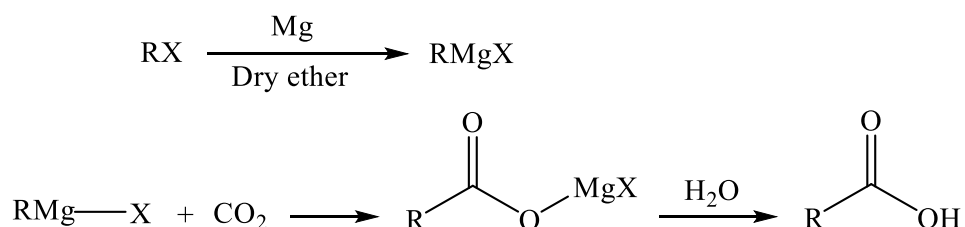
• **FROM ALKYL BENZENE:**

Also important is the oxidation of alkyl side chains of aromatic rings by strong oxidising agents such as chromic acid, potassium permanganate, and nitric acid to yield aromatic carboxylic acids. Regardless of the number of carbon atoms in the side chain or the presence of any groups attached to them, if the first carbon in the alkyl chain is bonded to at least one hydrogen (and not to another aromatic ring), all but one of the carbons are removed, and only a COOH group remains bonded to the aromatic ring.

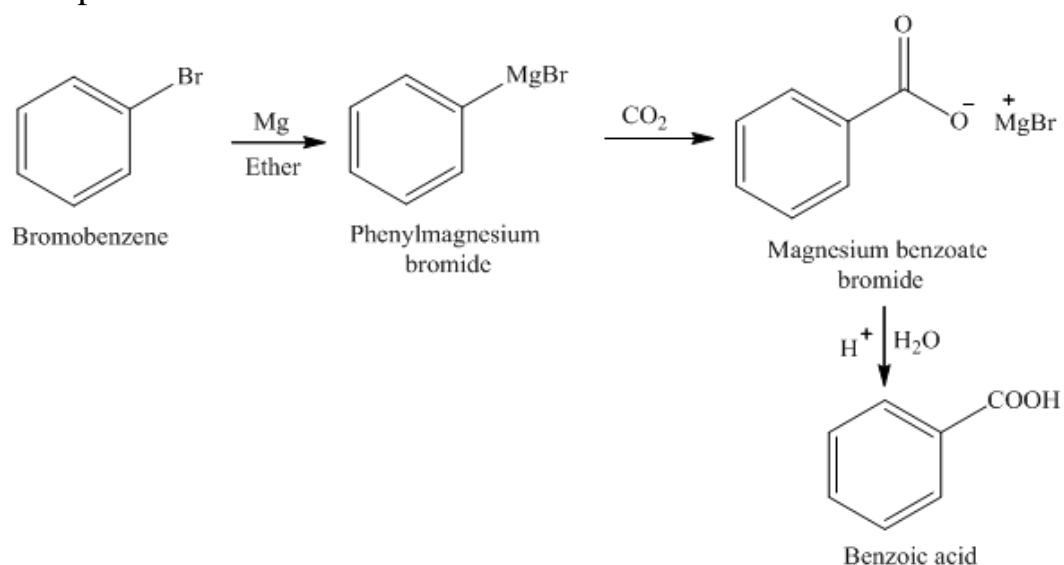


- FROM GRIGNARD REAGENTS:**

Grignard reagents react with carbon dioxide (either in the gaseous form, which is bubbled through the solution or as the solid dry ice) to give magnesium salts of carboxylic acids, which are converted to the acids themselves upon treatment with acid. Unlike the methods previously mentioned, this method adds one carbon atom to the carbon skeleton.



For example:



- FROM MALONIC ACID:**

Moreover, carboxylic acids can be prepared using malonic ester synthesis. Here, diethyl malonate is the most common example of malonic ester and useful to start with.

General reaction:

