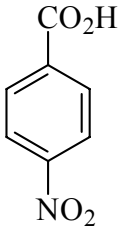
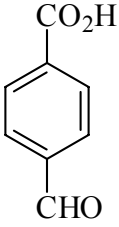
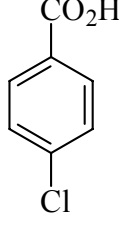
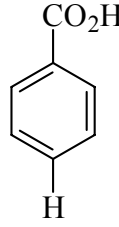
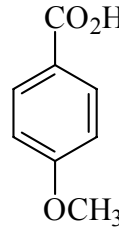


CARBOXYLIC ACIDS

Acidity:

- Carboxylic acids are the most acidic simple organic compounds (pKa ~ 5).
- But they are only weak acids compared to acids like HCl or H₂SO₄. (Remember the lower the pKa, the stronger the acid)
- Resonance stabilisation of the carboxylate ion allows the negative charge to be delocalised between the two electronegative oxygen atoms (compare with alcohols, pKa ~ 16).
- Adjacent [electron withdrawing substituents](#) increase the acidity by further stabilising the carboxylate (RCO₂⁻)

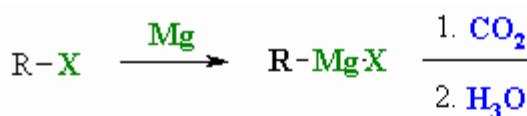
Carboxylic Acid	Structure	pKa
Ethanoic acid	CH ₃ CO ₂ H	4.7
Propanoic acid	CH ₃ CH ₂ CO ₂ H	4.9
Fluoroethanoic acid	CH ₂ FCO ₂ H	2.6
Chloroethanoic acid	CH ₂ ClCO ₂ H	2.9
Dichloroethanoic acid	CHCl ₂ CO ₂ H	1.3
Trichloroethanoic acid	CCl ₃ CO ₂ H	0.9
Nitroethanoic acid	O ₂ NCH ₂ CO ₂ H	1.7

					
pKa:	3.41	3.75	4.0	4.19	4.46

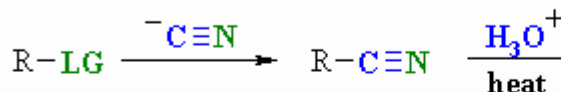
Preparations of Carboxylic Acids

(overview)

- [Carbonation of Grignards](#)



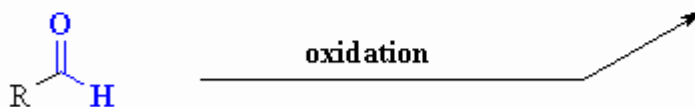
- [Hydrolysis of Nitriles](#)



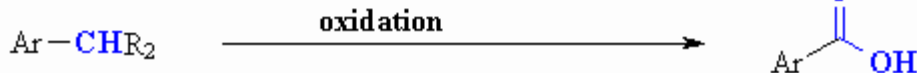
- [Oxidation of 1° Alcohols](#)



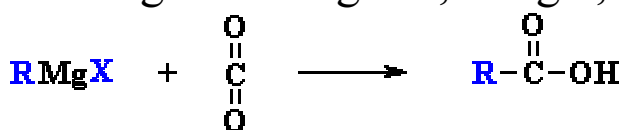
- [Oxidation of Aldehydes](#)



- [Oxidation of Alkyl Benzenes](#)



Carboxylation of Grignard Reagents, RMgX, by CO₂



Reaction usually in Et₂O or THF followed by H₃O⁺ work-up

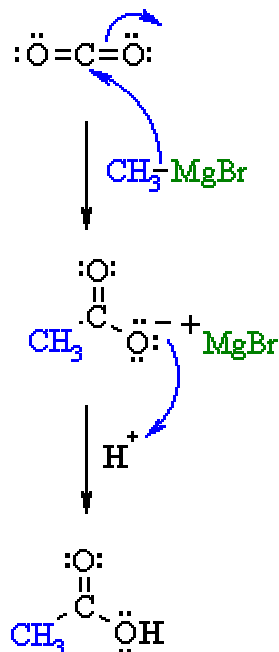
Summary

- [Grignard reagents](#) react with dry ice (solid CO₂) followed by aqueous acid work-up to give carboxylic acids.
- CO₂ can be thought of as being a dicarbonyl compound : O=C=O
- Note that the carboxylic acid contains one extra C atom compared to the original halide from which the Grignard reagent was prepared.

NUCLEOPHILIC ADDITION OF RMgX TO CARBON DIOXIDE

Step 1:

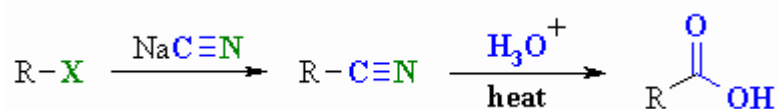
The nucleophilic C in the Grignard reagent adds to the electrophilic C in the polar carbonyl group, electrons from the C=O move to the electronegative O creating an intermediate magnesium carboxylate complex.



Step 2:

This is the work-up step, a simple acid/base reaction. Protonation of the carboxylate oxygen creates the carboxylic acid product from the intermediate complex.

Hydrolysis of Nitriles



Reaction type : Nucleophilic Substitution then Nucleophilic Addition then Nucleophilic Acyl Substitution !

Summary

- 1° and 2° [alkyl halides](#) (X = Cl, Br, I) or [tosylates](#) undergo [SN2 substitution](#) with cyanide salts to give nitriles.
- Nitriles can be hydrolysed to carboxylic acids without the isolation of the amide intermediate.
- Note that the carbon skeleton is extended by 1 C atom during this reaction sequence.
- Although aromatic nitriles cannot be prepared via the SN2 reaction, they too can be converted to the aromatic carboxylic acid by hydrolysis.