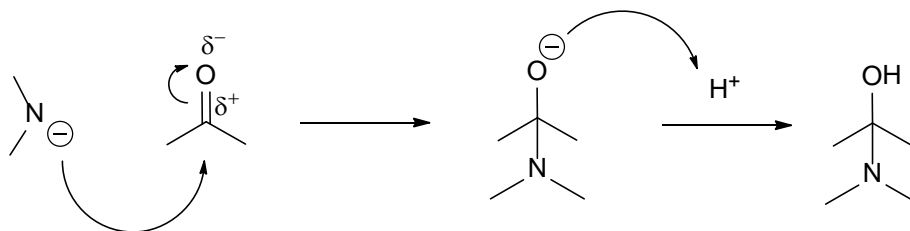


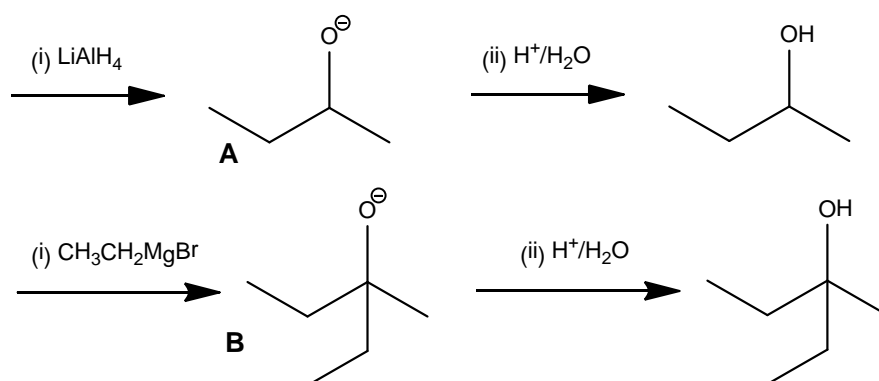
CHEM1902/4 Worksheet 7 – Answers to Critical Thinking Questions

The worksheets are available in the tutorials and form an integral part of the learning outcomes and experience for this unit.

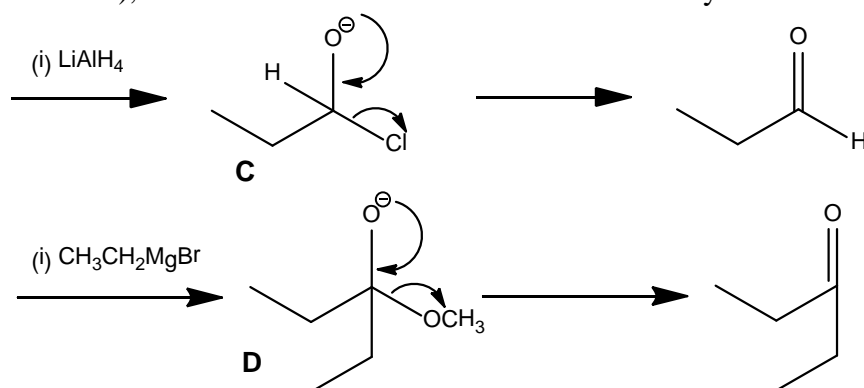
Model 12: Addition to a Carbonyl Group



1. See below.

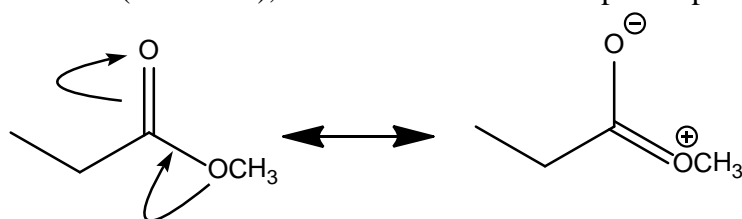


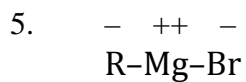
2. The first product is chiral and a racemic mixture will be produced. The second product is achiral.
3. Intermediates **C** and **D** have a leaving group attached to the tetrahedral carbon (the carbon-that-was-the-C=O), unlike **A** and **B** above. So **C** and **D** are likely to react as shown below, forming **E** and **F**.



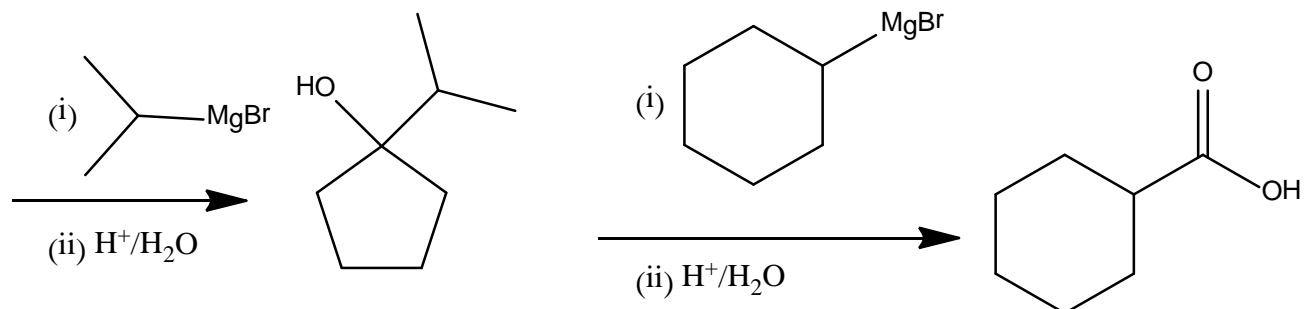
4. **E** is an aldehyde, **F** is a ketone. These are likely to react with the nucleophilic reagents present ($LiAlH_4$ and CH_3CH_2MgBr), so **E** would be reduced to the primary alcohol [$CH_3CH_2CH_2OH$], **F** converted to the tertiary alcohol [$(CH_3CH_2)_3COH$].

Aldehydes are more electrophilic than the corresponding esters. There is resonance stabilization of the ester (see below), which acts to reduce the partial positive charge on the carbonyl C atom.



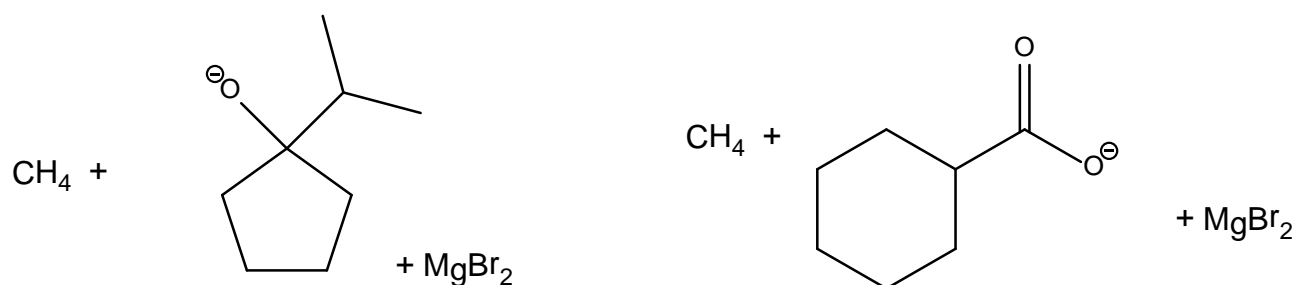


6. See below.



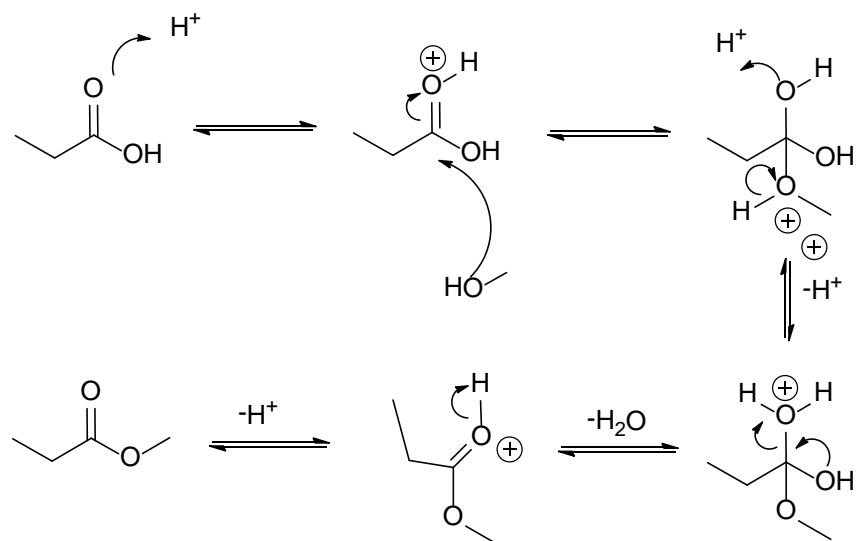
7. The acid converts the metal salt (ROMgBr and RCOOMgBr respectively) to the products shown. Grignard reagents act like $\text{R}-\text{MgBr}^+$: a carbanion is a very strong base and will react vigorously with any source of H^+ to produce RH and heat.

8. See below

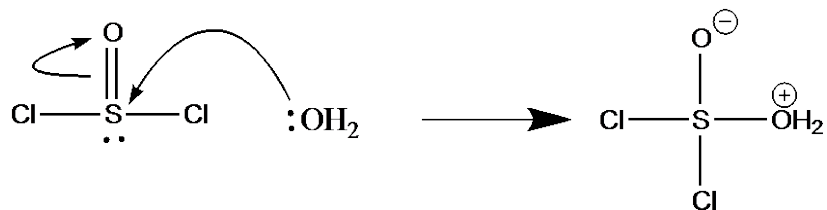


Model 13: Carboxylic Acid Derivatives

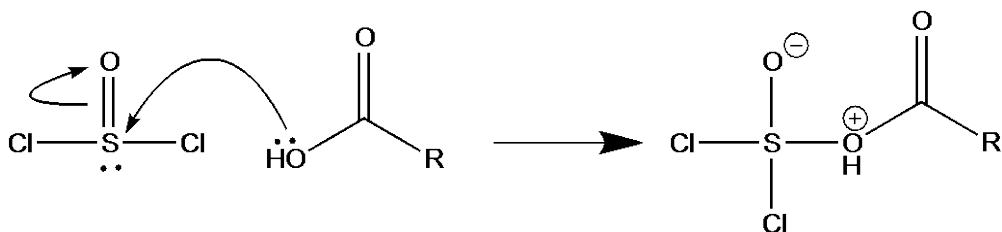
1. See below.



The Lewis structure of thionyl chloride, SOCl_2 , is shown below. The S has a significant δ^+ charge. It reacts with a nucleophile like water via nucleophilic attack of H_2O on the S atom:

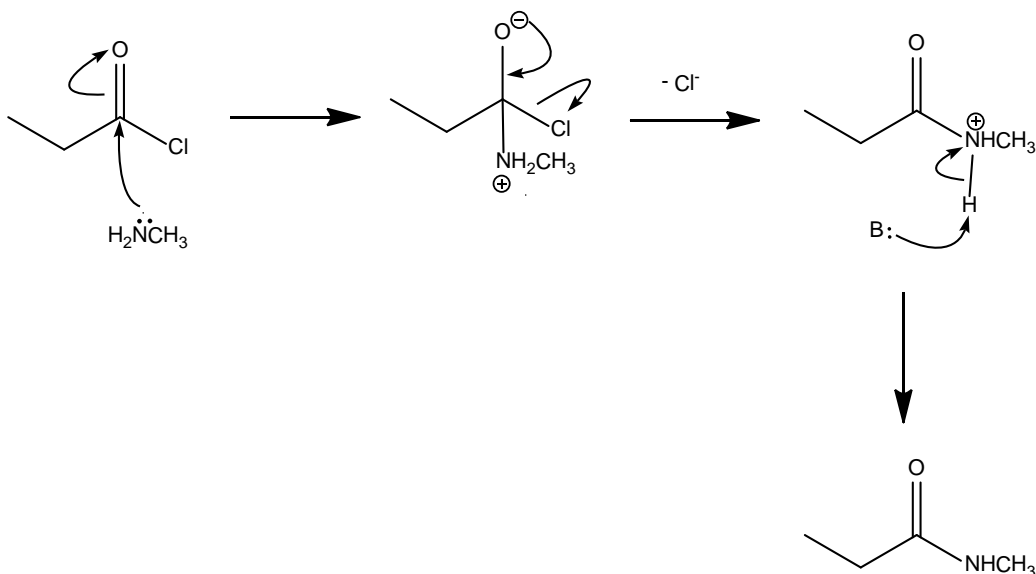


Ultimately, this leads to SO_2 and HCl . The first step of the reaction with carboxylic acids is similar:



Ultimately, this leads to SO_2 and RCOCl .

2. See below. The base, B, could be solvent or H_2NCH_3 .



3. The reactivity increases in the order:

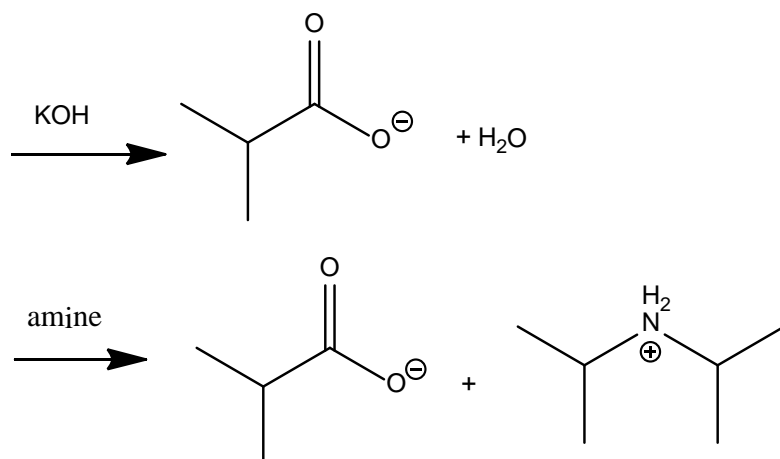
amides < acids ~ esters < anhydrides < acid chlorides

The resonance stabilization shown in Model 12 Q4 is key. As nitrogen is less electronegative than oxygen, it is more able to donate its lone pair and so the second resonance form is more important in amides than in acid anhydrides and esters.

The resonance stabilization requires good overlap of the p -orbital holding the lone pair and the $\text{C}=\text{O}$ π orbital.

As Cl is larger than O or N, the $\text{C}-\text{Cl}$ bond is long and the overlap of these orbitals is poor: little resonance stabilization occurs in the acid chlorides. The electron-withdrawing nature of the electronegative halide dominates increasing the δ^+ charge on the carbonyl carbon atom.

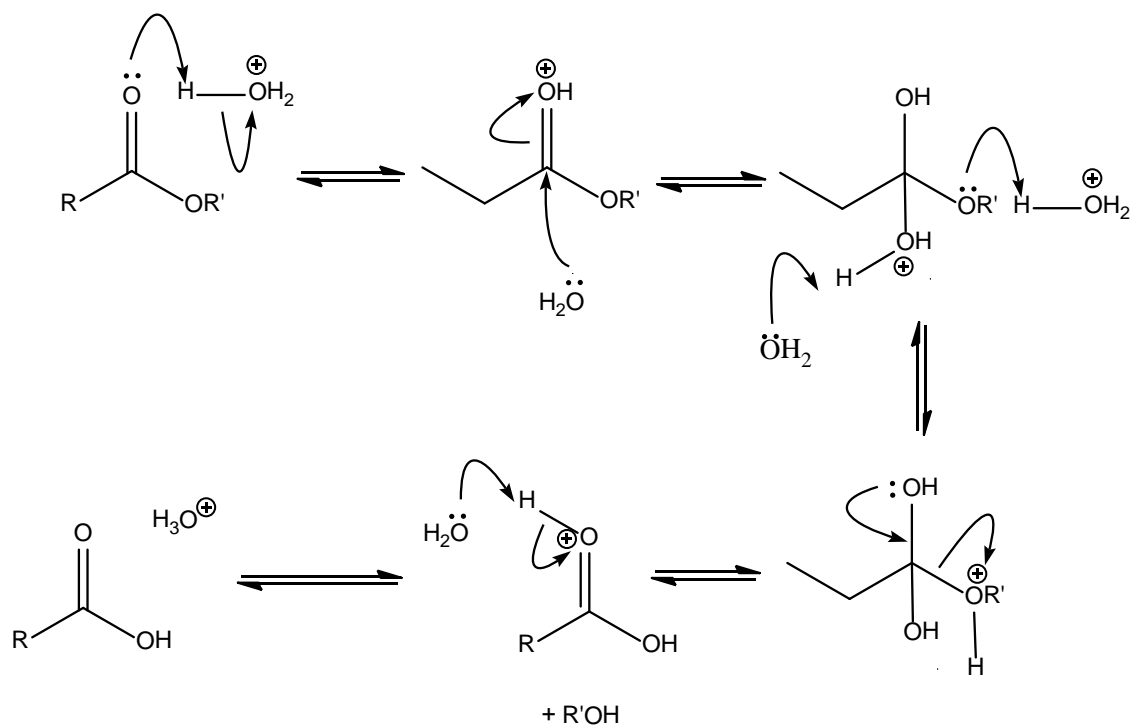
4. Brønsted acid / base H^+ transfer reactions occur:



Extension

An amine will react with a carboxylic acid in a simple acid-base reaction as shown in Q3. The amine will attack the most δ^+ atom in the carboxylic acid, which is the $-OH$ proton rather than the carbonyl carbon atom.

5. See below.



6. The steps are the reverse of those in the acid catalysed formation of an ester. As shown above, each step is reversible and it is possible to drive the reaction towards carboxylic acid + alcohol or towards ester by changing the conditions.

Extension

See below.

