Week 7-9
Carboxylic Acids

Preparation of Methyl 3-Nitrobenzoate
Preparation of 3-Nitrobenzoic Acid
Preparation of 3-Nitrobenzamide
Week 9
Preparation of 3-Nitrobenzamide

Figure 8.5. Preparation of an amide from a carboxylic acid.
Why Going Through Acyl Chloride?

**Acid - Base Chemistry**

![Chemical reaction diagram](image)
Mechanism of Acyl Chloride Formation

Mechanism 22.5  Conversion of Carboxylic Acids to Acid Chlorides

**Steps [1] and [2]** Conversion of the OH group into a good leaving group

$$\text{RCOOH} + \text{SOCl}_2 \rightarrow \text{RCOCl} + \text{HCl}$$

**Steps [3] and [4]** Substitution of the leaving group by Cl

$$\text{RCOCl} + \text{Cl}^{-} \rightarrow \text{RCl} + \text{SO}_2 + \text{Cl}^{-}$$
Mechanism of Amide Formation

Figure 8.7. Mechanism of amide formation from an acid chloride.
1st Step: Formation of Acyl Chloride

- Water bath needs to be 50 ± 5 °C
- Drying tube with CaCl₂
- 0.4 mL SOCl₂ (pipette)
- 0.5 g 3-nitrobenzoic acid
- 6 drops DMF
- Dimethyl FormAmide (DMF)
1st Step: Formation of Acyl Chloride

- Heat for 10 min, until everything has dissolved
- If after 10 min there is still solid add extra 0.2 mL SOCl₂
- Continue heating/stirring until no solid remains

mp = 135 °C

mp = 75 °C
2nd Step: Formation of Amide

Ice bath

12 mL NH₃ (15 M)
2nd Step: Formation of Amide

- Ammonia NEEDS to be cold! Keeping 1-2 pieces of ice in the ammonia solution during the addition will help to keep the temperature close to 0 °C.

Add the reaction mixture drop wise, slowly! (1 drop / 2 sec)
2nd Step: Formation of Amide

What if you do a quick addition?

\[ \text{NH}_3 = 30\% \text{NH}_3, 70\% \text{H}_2\text{O} \]

- At low temperature, \( \text{NH}_3 \) reacts faster than \( \text{H}_2\text{O} \):

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{Cl} \\
\text{O} & \\
\text{O}_2\text{N} & \quad \text{NH}_2
\end{align*}
\]

- If the temperature is higher, the \( \text{H}_2\text{O} \), which is in excess will react too!!!
3rd Step: Amide recrystallization

1. Dissolve product in minimum amount of EtOH
2. Add water drop wise until it gets cloudy. Then add one drop of EtOH

Collect crystals

Cool down

Collect amide with suction filtration

Wash several times with water to remove NH₄Cl
Report all yields (weeks 7-9) and melting points!

Submit all products in properly labeled vials for full credit.

The glassware for next week's experiment must be completely dry. Clean the following equipment and place them in a labeled 250 mL beaker and dry them thoroughly in an oven for 30 minutes. Make sure to take the hot glassware out of the oven and place them in your drawer before exiting from the lab; you may risk losing them forever. The estimated replacement cost is approximately $100.

8 mL vial, 5 mL vial, Claisen adapter, air condenser, drying tube, glass stirring rod, and triangular stir bar.