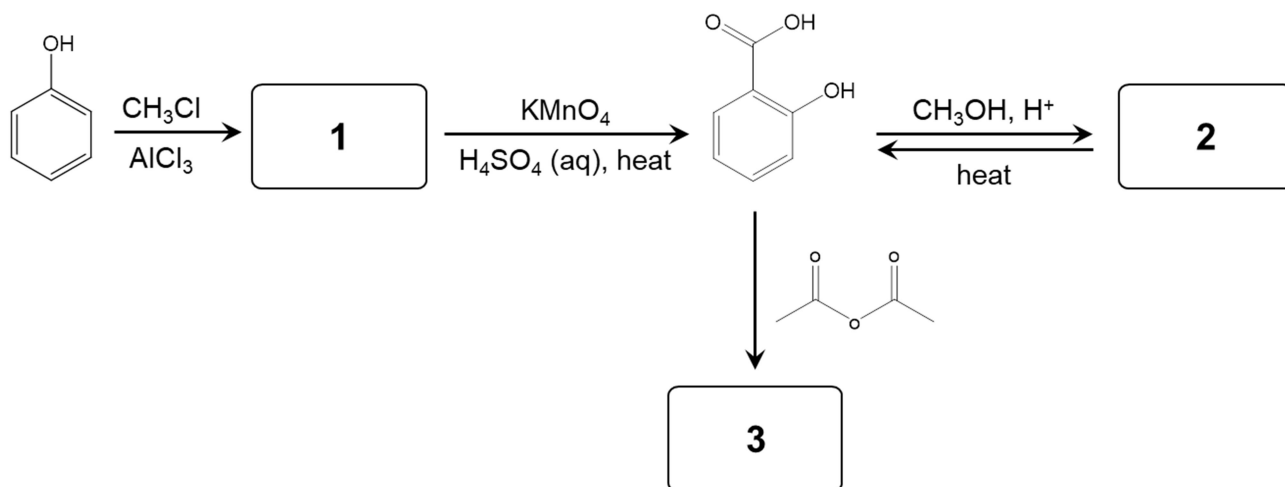


### Exercise n°4



Find the structure of the compounds **1**, **2** and **3** and write their names. Be careful about the possible reaction on different functional groups (called *chemoselectivity*): the stronger nucleophile reacts with the stronger electrophile.

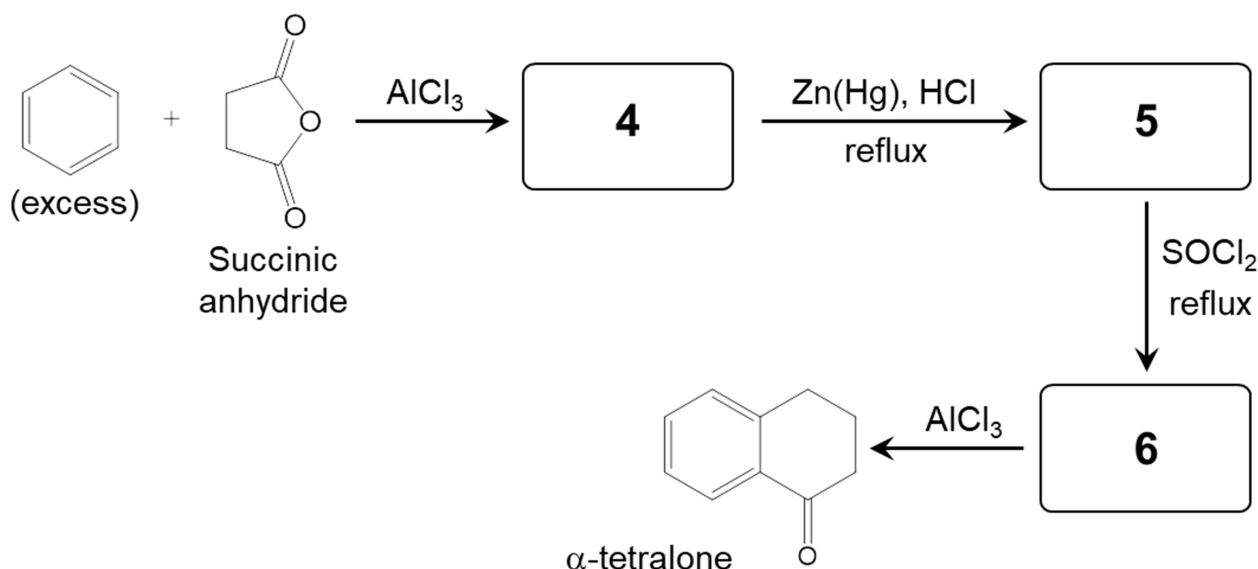
Write all the steps involved in the first reaction and justify the direction of the attack (ortho, meta or para). Highlight the possible formation of by-products of the reaction and describe possible troubles in his synthesis.

Compound **2** is a pheromone produced by plants as an anti-herbivore defence. If the plant is infected with herbivorous insects, the release of **2** may function as an aid in the recruitment of beneficial insects to kill the herbivorous insects.

Compound **3** is a nonsteroidal anti-inflammatory drug (NSAID) used to treat pain, fever, or inflammation and also used long-term to help prevent heart attacks, ischaemic strokes, and blood clots in people at high risk.

### Exercise n°5

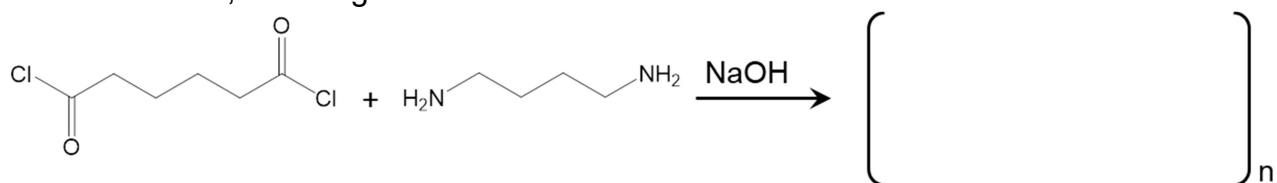
$\alpha$ -tetralone is the starting molecule for the synthesis of insecticides, beta-blockers as well as for the antidepressants and anti-protozoan therapeutics. It can be prepared from benzene and succinic anhydride in a multi-step synthesis.



Write the structure of compounds **4**, **5** and **6**. Explain why the first reaction stops at the monosubstituted compound (differently from the reaction leading to **1**).

### Exercise n°6

Polymers are molecules made by a continuous chain of repeating units, called monomers. Nylon (6,6) is a polymer synthesized by reaction of adipoyl chloride with 1,6-diaminohexane, following the next reaction:

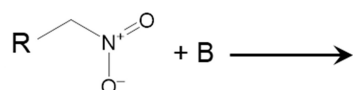


Answer to the following questions:

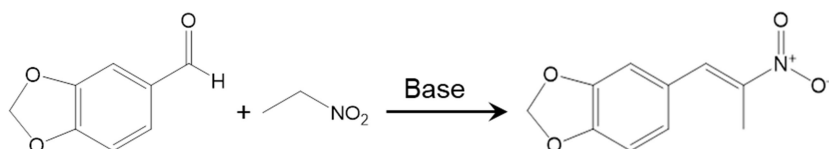
1. Identify the repeating unit of Nylon (6,6);
2. Which kind of reaction is involved in the formation of Nylon (6,6)?
3. Which is the role of  $\text{NaOH}$ ? Which by-products are formed by the reaction?

## Exercise n°7

The  $\alpha$ -hydrogen of nitroalkanes are appreciably acidic ( $pK_a = 10$ ), much more acidic than those of aldehydes and ketones. The acidity of these hydrogen atoms, like the  $\alpha$ -hydrogens of aldehydes and ketones, can be explained by the powerful electron withdrawing of the nitro group and by resonance stabilization of the anion that is produced. Write the resonance forms of the anion produced by the following reaction:

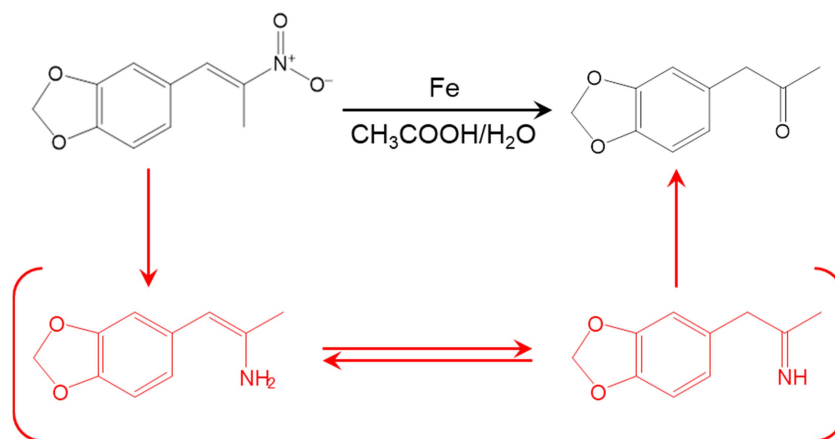


Nitroalkanes that have  $\alpha$ -hydrogens undergo base-catalysed condensation with aldehydes and ketones that resembles the aldol condensation. This is a key step in the synthesis of MDMA (3,4-Methylenedioxyamphetamine). The first step is the condensation of piperonal with nitroethane, catalysed by a base.



Write a plausible mechanism for this reaction that resembles that of aldol condensation.

The second step of MDMA synthesis is the treatment of the nitrocompound obtained in the first one with a mixture of Fe, CH<sub>3</sub>COOH and H<sub>2</sub>O. The product is obtained in three steps, following the sequence highlighted in red (intermediate species cannot be isolated). Identify which type of reaction is each step of this sequence.



The synthesis of MDMA is completed by other 2 consecutive steps, as drawn below. For each step, identify which kind of reaction is and which reagents or catalysts must be employed.

