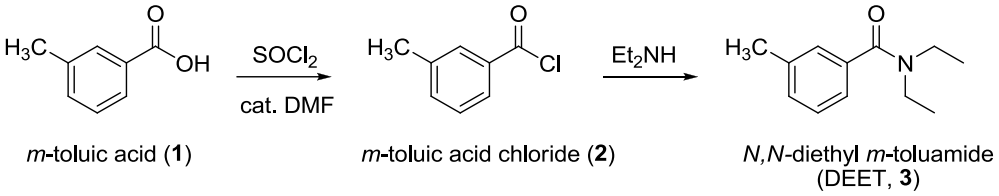
The first laboratory course in **Organic chemistry** in English **(PB)**

Part 1: **Synthesis of DEET**



m-toluic acid (**1**) *m*-toluic acid chloride (**2**) *N,N*-diethyl *m*-toluamide (DEET, **3**)

Scheme 1. Outline of synthetic steps.

DEET (**3**) is a common mosquito repellant that you can buy in one form or another in most general stores. It is one of those chemicals that not only saves us from the inconvenience of being bitten but also allows to control the spread of very serious diseases such as malaria. Here you will attempt to synthesize DEET (**3**) with isolation of the intermediate acid chloride **2.**

You will start with 15 g of 3-methyl benzoic acid (**1**). You will have to vacuum distill both **2** and **3**. Your objective is also to search for the appropriate scientific publication, in which the synthesis or physical properties of the compounds are described. The following databases are available on campus (or through a proxy service):

1. www.reaxys.com
2. www.scifinder.cas.org (you might have to register using your student e-mail address)

Both these databases allow you to search for a phrase, a structure or a reaction. Use them to your advantage.

You are going to follow the reaction sequence presented in Scheme 1. If you experience problems finding the appropriate publication on the synthesis according to the scheme you could look for a procedure for a similar compound, *e.g*. with a methyl group at a different position or even without the 3-methyl group. Be aware that you nonetheless have to find the physical data for the needed compound, as well as all the reagents used. You need to familiarize yourself with the techniques to be used, and with the dangers of using the necessary reagents. This has to be done **prior** to the laboratory class.
Should you have any doubts please do not hesitate to contact your TA in room **207, bld. A2**.

As for the first step, you could find the following links to publications helpful (note that only a small portion of the paper – at most several lines - is relevant to your experiment):

http://onlinelibrary.wiley.com/doi/10.1002/1521-3897(200009)342:7%3C642::AID-PRAC642%3E3.0.CO;2-A/abstract

http://pubs.acs.org/doi/pdf/10.1021/jo01067a669

You can find ^{1}H and ^{13}C NMR spectra of **3** in $CDCl_3$ here:

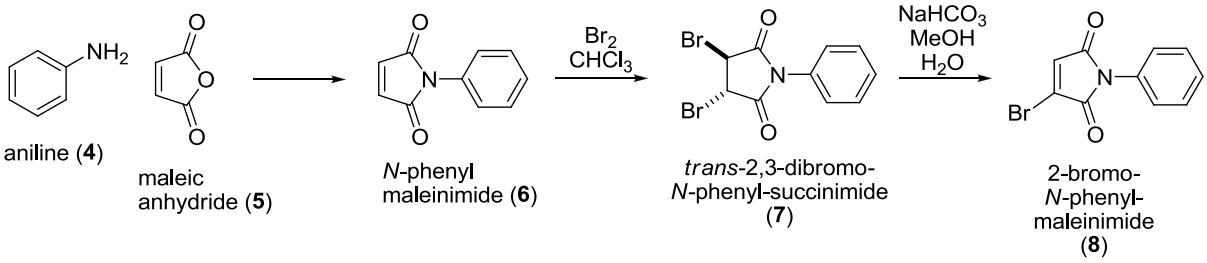
http://org.wch.pwr.edu.pl/studnt_DEET.zip

The Zip-file contains data directly obtained from a 600 MHz spectrometer.

Once you unpack the contents of the archive, you can open them with an academic version of ACD/NMR Processor. It can be obtained here:

http://www.acdlabs.com/resources/freeware/nmr_proc/

Part 2: **Synthesis of 2-bromo-*N*-phenyl-maleinimide**



Scheme 2. Outline of synthetic steps.

Vinyl bormides are useful intermediates in many synthetic pathways. Unlike alkyl halides they are not electrophilic, but can easily undergo halogen-metal exchange reactions, including Suzuki or Heck couplings.

Your assignment is to prepare one such compound – **8**. Try to plan your synthesis to obtain 5 g-amount of your product. You will need to consult a few research papers to do so. Make sure that the procedures you find call for the reagents shown in Scheme 2.

Here are some links that you might find useful (but not all):
http://pubs.rsc.org/en/Content/ArticleLanding/2014/CC/C4CC02107J#!divAbstract
http://pubs.rsc.org/en/Content/ArticleLanding/2011/CC/C0CC04115G#!divAbstract