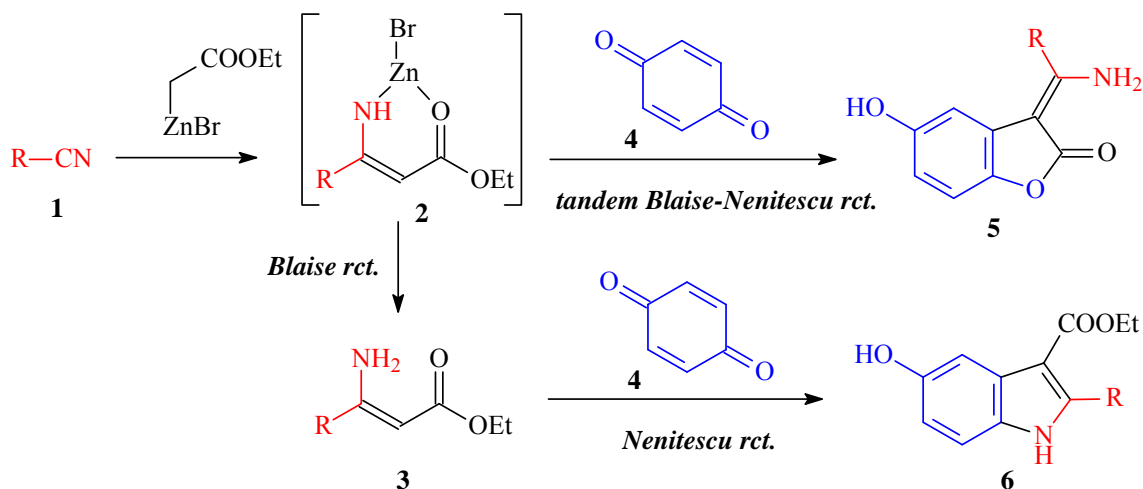


Organic Chemistry
Day 1 – 25.02.2011

Problem 1.

In a recent paper, Chun and coworkers obtained 5-hydroxy- α -(aminomethylene)-benzofuran-2(3*H*)-ones from nitriles in a tandem Blaise-Nenitescu reaction. The graphical abstract of this paper outlines the general processes:



Y.S. Chun, K.Y. Ryu, J.H. Kim, H. Shin, S. Lee, *Org. Biomol. Chem.*, **2011**, 9, 1317-1319

- Write the mechanism of the classic Nenitescu synthesis of indole (the transformation **3** \rightarrow **6**);
- Propose a suitable pathway for the tandem Blaise-Nenitescu synthesis of 5-hydroxy- α -(aminomethylene)-benzofuran-2(3*H*)-ones (the transformation **2** \rightarrow **5**);

Problem 2.

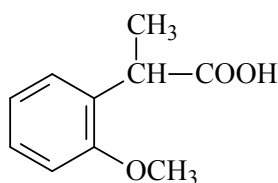
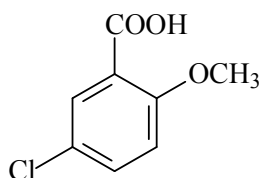
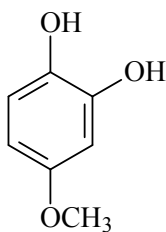
The hydrocarbon C_6H_{12} presents, in its NMR spectra, the following signals (δ , ppm):

5,84 (q, 1H), 4,93 (q, 1H), 4,82 (q, 1H) and 1,01 (s, 9H).

- Identify this hydrocarbon and propose two different preparations for it, one starting from acetone and the other through a Wittig olefination.
- Write the reaction of this hydrocarbon with hydrochloric acid.

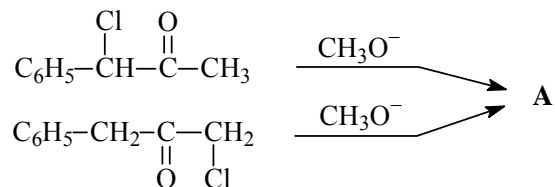
Problem 3.

Prepare the following compounds:



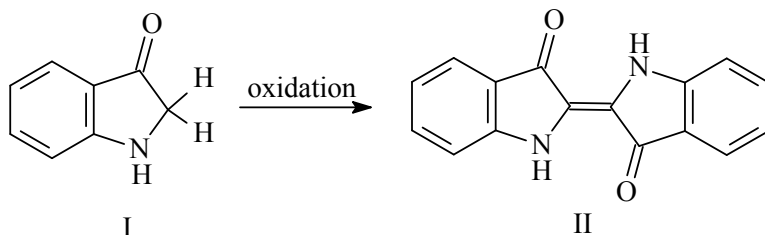
Problem 4.

What is the reaction product **A** for the following transformation. Propose the reaction mechanisms.



Problem 5.

Indigo (II) is one of the most famous dyes, used in different cultures for more than 4000 years. It can be obtained starting from indoxyl (I) by oxidation.



Indoxyl can be synthesized by reacting anthranilic acid or aniline with chloroacetic acid and the obtained glycol derivatives are cyclised by alkaline fusion using alkaline hydroxides. Explain, using reaction mechanisms, the behavior of the two glycol derivatives.

*Correct answers to each problem will be noted with **6 points** for a total of **30 points**.
 All correct answers that are proposed will be noted accordingly.*