## QUESTIONS / EXAM 15.12.2021

## Course : REACTIVITY OF AROMATICS

Code : CHEM-E4160
Date / time : $\mathbf{1 5 . 1 2}$ klo 9.00-13.00

## Question 1 (10p)

Please read carefully the following hints, and draw the mechanism for the reaction below; "The starting material first tautomerizes to the keto-enol. Protonation of the ketone then gives a very stable carbocation, to which EtOH adds. Deprotonation of the nucleophile, protonation of the OH leaving group, and following loss of water gives a new carbocation, which undergoes a fragmentation reaction with loss of $\mathrm{H}^{+}$to give the enol ether product"


## Question 2 (10p) :

a) 2-Aminopyridine is chlorinated by reaction with chlorine in $17 \%$ aqueous sulfuric acid. 2-Amino-5-chloropyridine and 2-amino-3,5-dichloropyridine are formed in a 1:1 ratio. As the concentration of the sulfuric acid is increased, the proportion of-2-amino-5-chloropyridine increases, until in $72 \%$ sulfuric acid it is formed almost exclusively (and is isolated in $82 \%$ yield). Suggest an explanation ?
b) Predict the product of nitration of pyridazine 1-oxide (using a mixture of nitric and sulfuric acids) ? [The structure and reactivity of pyridine N -oxide can be found in the lecture material. In the pyridazine structure two nitrogen-atoms can be found in the heterocycle next to each other]

## Question 3 (10p) :

a) This unsaturated alcohol will become a bicyclic compound immediately when treated with $\mathrm{Cr}(\mathrm{VI})$. Why ?

b) The following heterodienophiles (1-3) react with different dienes in a Diels-Alder cycloaddition to obtain products $A, B$, and $C$, respectively. What are the structures of these dienes ? The dienophile 4 reacts with diene 5 to obtain either D or F. Which of these two products is formed and why ? [Hint : The pyridine ring is formed via an elimination-step !]



## Question 4 (10p)

This is a very interesting 7-membered ring-formation. How do you think that the ring is formed ? [Hint: Consider a Michael addition as the first step]


## Question 5 (10p)

How is this fused indole-structure formed ? Please write a possible mechanism, or explain in own words how the reaction most probably will proceed ?


