

QUESTIONS / EXAM 9.12.2020

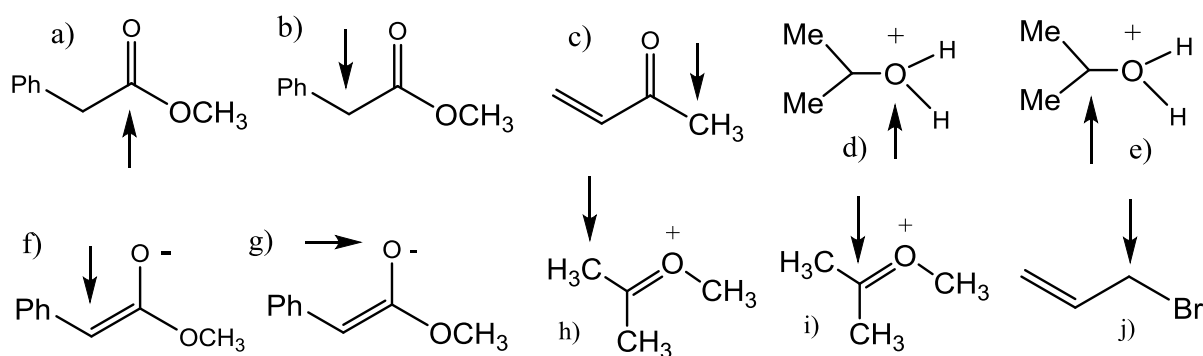
Course : **REACTIVITY OF AROMATICS**

Code : **CHEM-E4160**

Date / time : **9.12 klo 9.00 – 12.00**

Question 1 (10p)

The first question is about nucleophilicity and electrophilicity, an important thing not only in case of reactivity of aromatics. Is the position (the atom indicated) in these molecules nucleophilic or electrophilic ?

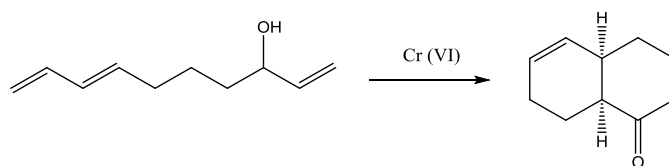


Question 2 (10p) :

- 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 ?
- 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]

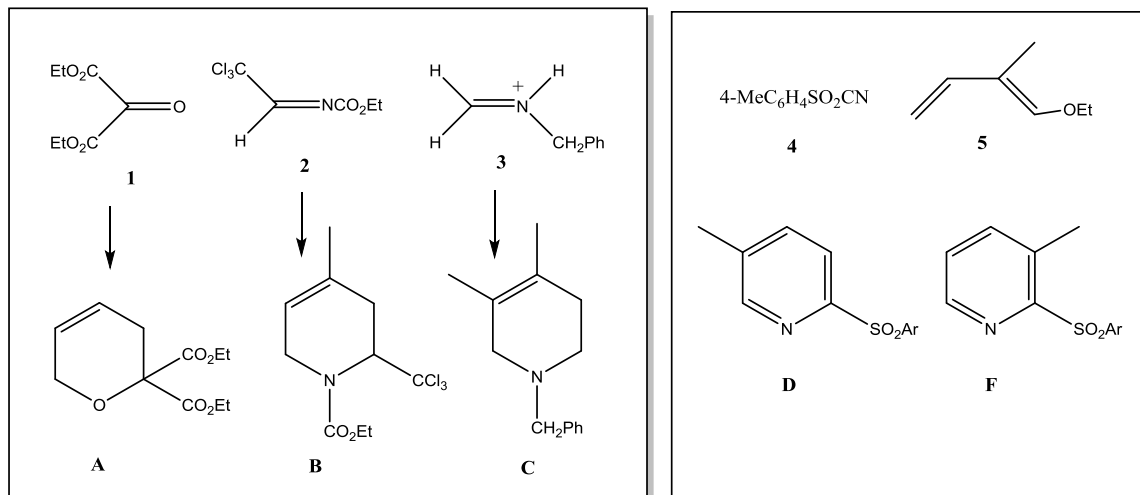
Question 3 (10p) :

- This unsaturated alcohol will become a bicyclic compound immediately when treated with Cr(VI). Why ?



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- 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? [Hints : 1. Observe that there is a cyano-group in compound 4. 2. The pyridine ring is formed via an elimination-step]



Question 4 (10p)

- Is it possible to brominate further 2,4,6-tribromophenol if we use bromine in acetic acid? Account for the formation of the product in that case? What happens to the aromatic ring?
- Substituted phenols have very different pK_a values depending on the substituents attached to the aromatic ring. Consider the following compounds : i) Phenol ii) p-nitrophenol iii) o,p-dinitrophenol iv) m-chlorophenol, and v) 2,4,5-trimethylphenol. Which of the compound has the lowest pK_a value (about 4) and which the highest (about 11)? Suggest with explanations for order of the pK_a values, if we list these in order from smallest pK_a value to highest?
- How would you synthesize via two steps these simple aromatic compounds from benzene :
m-bromobenzenesulfonic acid
p-bromobenzenesulfonic acid*
m-chloronitrobenzene

* Why is it difficult to obtain p-bromobenzenesulfonic acid in good yield and purity using this reaction sequence ?

Question 5 (10p)

How is this fused indole-structure formed? If possible, please add a picture taken by your camera and added to show the mechanism, or explain in own words how the reaction most probably will proceed?

