FRO-II 2021 QUESTIONS OF THE WEEK 4 - SOLUTIONS

1)

$$\begin{array}{c} \bullet & \bullet \\ \bullet & \bullet \\$$

EWG subtituent destabilizes the σ -complex when -E is in *ortho*- or *para*-position, so *meta*-product is the least deactivated and is formed preferentially; the reaction is slower than compared to benzene. -CO₂Me is an EWG making the S_EAr more difficult.

EDG subtituent stabilizes the σ -complex when -E is in *ortho* or *para*-position, so *meta*-product is the least activated, *ortho*- and *para*-products are formed preferentially. The ratio between the *ortho*- and *para*-products is controlled by the steric hindrance of the EDG. The reaction is faster than compared to benzene. -NMe₂ is an EDG making the S_EAr easier.

2)

$$\begin{array}{c|c} & \text{HNO}_3 \text{ conc} \\ & \text{H}_2 \text{SO}_4 \text{ conc} \\ \hline & & \text{NO}_2 \\ \hline & & \text{FeBr}_3 \\ \hline & & \text{or H}_2, \text{Pd/C} \\ \hline & & \text{orly mono-substituted} \\ \end{array}$$

3) A)

B)

Ring 2 is more reactive than **ring 1** because it contains only activating group (aryl ether), that stabilizes the σ -complex. Therefore electrophilic substitution occurs on **ring 2** with *ortho-* / *para*-orientation (*para*-substituted product is major for steric reasons).