Ch41b: Quiz #4

1. Circle the appropriate word, indicating whether the molecule shown undergoes bromination faster or slower than benzene. (16 points)

![Diagram with molecular structures and options for faster or slower bromination](image-url)
2. Rank the following aromatic compounds in order of increasing reactivity toward nucleophilic aromatic substitution (i.e., 1 = least reactive, 5 = most reactive). Explain briefly, using resonance structures if appropriate. (15 points)

\[ \text{NO}_2 \text{F} \quad \text{NO}_2 \text{F} \quad \text{NO}_2 \text{F} \quad \text{NO}_2 \text{F} \quad \text{NO}_2 \text{F} \]

\[ 1 \quad 4 \quad 3 \quad 5 \quad 2 \]

- **Stabilized by the two nitro groups**
  - \( \text{NO}_2 \text{F} \) (2)

- **Stabilized by the one nitro group**
  - \( \text{NO}_2 \text{F} \) (1)

- **Stabilized by the one nitro group but is sterically hindered**
  - \( \text{iPr}_2 \text{NO}_2 \text{F} \) (3)

- **No extra resonance stabilization, but is inductively stabilized**
  - \( \text{NO}_2 \text{F} \) (4)

- **OMe destabilized transition state**
  - \( \text{OMe} \) (5)
3. Predict the major product(s), if any, of the following reactions: (14 points)

(1) 

This reaction goes through a benzyne mechanism, giving two isomers.

(2) 

The fluoro group is displaced in an $S_N Ar$ mechanism.

Nuc. addn step = rate limiting
C-F bond more electrophilic
Thus preferentially attached
4. The amount of anti-addition in the chlorination of alkenes varies with the structure of the alkene, as shown in the table below. Formation of the anti-product proceeds through a chloronium ion intermediate. (15 points)

\[
\begin{align*}
\text{R} & \quad + \quad \text{Cl}_2 & \quad \rightarrow & \quad \text{R} \quad \text{H} \quad \text{Cl} \quad \text{Cl} \\
\text{H}_3\text{C} & \quad \quad \quad & \quad & \quad 99 \\
\text{Ph} & \quad \quad \quad & \quad & \quad 88 \\
\text{H}_3\text{CO} & \quad \quad \quad & \quad & \quad 63
\end{align*}
\]

Suggest a reason for the variation in the stereochemistry of addition as the alkene structure is varied.

The phenyl group and p-methoxy phenyl group can stabilize via resonance donation the cation formed from opening the halonium intermediate. The p-methoxy phenyl group is a stronger resonance donor than the phenyl group, thus further favoring the open intermediate. The open intermediate leads to equal amounts of *syn* and *anti* product.

Sterics and inductive arguments are not valid answers.