(a) (i) Standard curly arrow mechanism and energy profile diagram with 1st transition state rate limiting. Energy of starting material higher than product (reaction is exothermic overall). Meisenheimer intermediate is a lot higher in energy than the starting material due to loss of stabilisation due to aromaticity but is an energy minimum because stabilised by resonance. Rate limiting 1st transition state (maxima) during formation of C-O bond, non-rate limiting 2nd transition state (maxima) during breaking of C-Cl bond.

![Energy profile diagram](image)

Essentially straight from the notes. Anticipated marking scheme: 2 marks for correct curly arrow mechanism. 1 mark for profile and axes. 1 mark for annotated transition states and intermediate.

(4 marks)

(ii) The negatively charged Meisenheimer intermediate is too high energy to form unless the negative charge can be stabilized by resonance with the cyano group which when situated ortho or para to the ‘leaving group’ is able to accept the electron density onto its nitrogen atom.

![Resonance forms](image)

Application of concepts from notes/lectures. We did not discuss this specific reaction but we did discuss S_{2}Ar reactions. Anticipated marking scheme: 2 marks for correct resonance forms for Meisenheimer intermediate.

(2 marks)
(iii) $S_N$Ar reactions are under kinetic control. The rate determining step is attack of the nucleophile (i.e. methoxide in this case) on the ipso-carbon of the ‘leaving group’.

Essentially straight from the notes but applying to an unseen reaction.

(1 mark)

(iv) The so-called ‘element effect’ tells us that the more electronegative the ‘leaving group’ the more electrophilic the ipso-carbon and so the lower the energy of the 1st transition state for reaction at that position and the faster the reaction. Therefore, switching the chlorine for a fluorine should lead to a faster reaction.

Essentially straight from the notes but applying to an unseen reaction.

(1 mark)

(b) The expected major product of the reaction is:

\[
\begin{array}{ccc}
\text{m-directing} & \text{CO}_2\text{Me} & \text{SO}_3 \ (g) \\
\text{o/-p-directing} & \text{OMe} & \text{c}_2\text{H}_5\text{SO}_2 \\
\end{array}
\]

The electrophile is protonated SO3 and the S$_E$Ar mechanism is required. Regiochemistry follows from the methoxy group lone pair conjugation directing o/p at the same time as the ester directing m- - hence reinforcing the indicated regiochemistry.

Problem Solving – this specific reaction was not discussed in lectures although sulfonylation and directing group effects were. Anticipated marking scheme: 2 marks for correct product, 2 marks for S$_E$Ar mechanism and half a mark for discussion of relative strengths of directing effects.

(4.5 marks)

(c) The mechanism and expected major product of the reaction is:

This is a Sandmeyer nucleophilic substitution reaction in which the diazonium salt accepts an electron from the copper(I) salt to give a copper(II) salt and diazo radical. This radical fragments to evolve molecular nitrogen and a phenyl radical which recombines with a bromine atom from the copper(II) salt to regenerate the copper(I) bromide. The regiochemistry is assured as ipso substitution. An alternative method would be to use KBr – but this would proceed via an $S_N1$ mechanism.

Problem Solving – this specific reaction was not discussed in lectures although Sandmeyer reactions and their mechanism was. Anticipated marking scheme: 1 mark
for correct product, 2 marks for correct arrows for the reaction including radical intermediate, half a mark for noting a mechanism enforced *ipso*-substitution and 1 mark for noting KBr or NaBr as alternative reagents for this transformation (*via* a different mechanism).

*(4.5 marks)*