Nitration of Phenylacetonitrile

**Question:** Is the \(-\text{CH}_2\text{CN}\) group an \(o,p\) director or a \(m\)-director? Does the nitration of phenylacetonitrile lead to the ortho, meta, or para product as the major product?

**Reading:** Read up on electrophilic aromatic substitution (specifically nitration of benzene) in your organic textbook (Klein, Chapter 19, section 19.4, mechanism 19.5). Also, read up on activating vs. deactivating groups, \(o,p\) vs. \(m\)-directors (Klein, Chapter 19, sections 19.7-19.10).

**Background:** Electrophilic aromatic substitution allows us to add a variety of functional groups directly to a phenyl ring. Such reactions include halogenation, sulfonation, alkylation, and acylation. In this lab, we will perform a nitration, or addition of the \(-\text{NO}_2\) substituent.

![Nitrated Phenylacetonitrile](image)

If an aromatic compound has one substituent, nitration could potentially occur at the ortho, meta, or para position (giving a 1,2-, 1,3-, or 1,4-product.) The identity of the major product is controlled by the identity of the original substituent on the substrate; some groups are said to be \(o,p\)-directors, while others are \(m\)-directors. In this experiment, you will determine the identity of the major product of the nitration of phenylacetonitrile and use this data to label the \(-\text{CH}_2\text{CN}\) group as either an \(o,p\)-director or \(m\)-director.

**Procedure:** In a small Erlenmeyer flask cooled in an ice bath in the hood, 3 mL of sulfuric acid is added slowly to 3 mL of concentrated nitric acid. Phenylacetonitrile (1.0 mL) is added to the acid dropwise with a Pasteur pipet over five minutes. (Gently and continuously swirl the flask in the icebath during the addition to maintain a low temperature.) After the addition is complete, remove the flask from the icebath and allow to stand at room temperature for one hour. Slowly pour the solution onto crushed ice in a beaker (~40g) and stir with a glass rod until the ice is melted. Filter the solid that forms by suction filtration and wash the product well with cold water. Transfer the crude moist solid to a small beaker and add a mixture of 5 mL ethanol/2 mL distilled water. Heat the covered beaker with stirring until the solid dissolves, then allow the product to recrystallize. Filter the product, allow to dry, and obtain a melting point. Collect all filtrates as waste in a container in the waste hood.

**Comments:**
What is the major product formed in this reaction? What data support this claim? If you had taken a C-13 NMR, would it be helpful in distinguishing ortho, meta, and para products? If you had taken a proton NMR, would the data be helpful? Based on your data, is the \(-\text{CH}_2\text{CN}\) group electron donating or electron withdrawing? Is it an \(o,p\)-director or \(m\)-director? Draw a mechanism for formation of the major product in this reaction and explain why this mechanism is favored over one of the other possibilities.

**Lab 8 assignment:** Turn in a hardcopy of your lab notebook (carbon copy or photocopy)
- Due at the beginning of lab next week
- 25 pts based on in-lab performance, completion of all sections, correctness of content