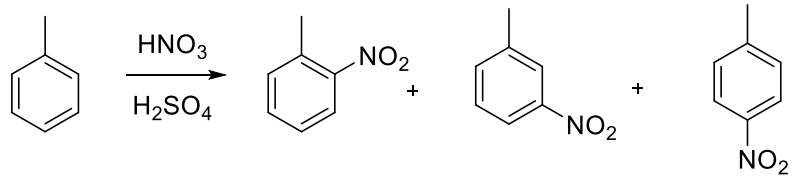
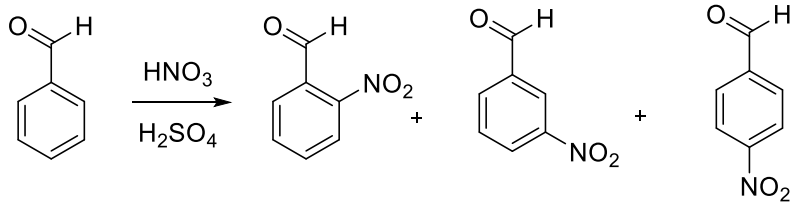
THE VIRTUAL ARYL NITRATION AND ACYLATION

In this virtual experiment, you will explore the electrophilic aromatic substitution (EAS) reaction and Friedel-Crafts Acylation of toluene and benzaldehyde. You will further compare the different directing groups to explain ortho/meta/para products.

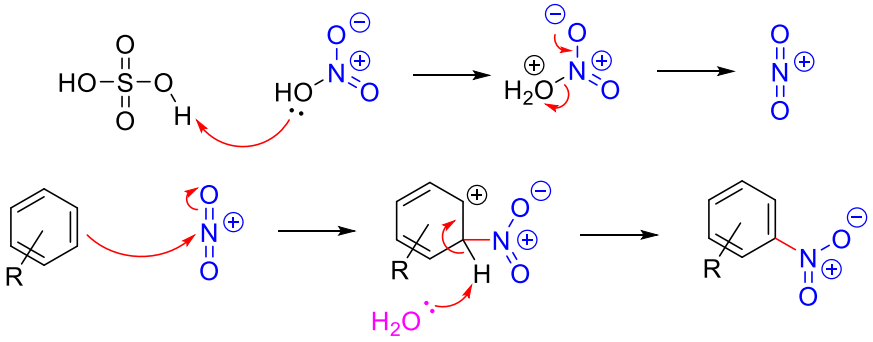
Introduction

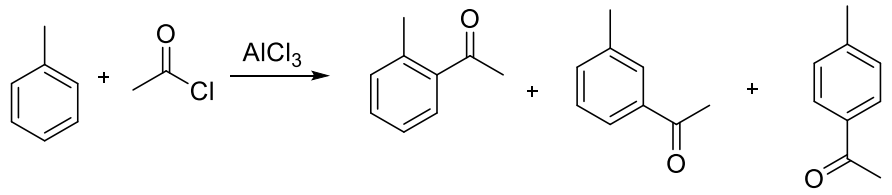
The rate of an electrophilic substitution reaction on a substituted benzene ring can either be faster or slower than that of benzene, depending upon the nature of the inductive and resonance effects of the attached group. In addition, the attached group will preferentially direct an incoming substituent primarily ***ortho/para*** or ***meta***, depending on the nature of the attached group. Review the appropriate chapters from your textbook to ensure that you understand the reasons for the activating/deactivating, and directing effects of various groups, including the resonance structures of the intermediates formed during the course of the reaction.



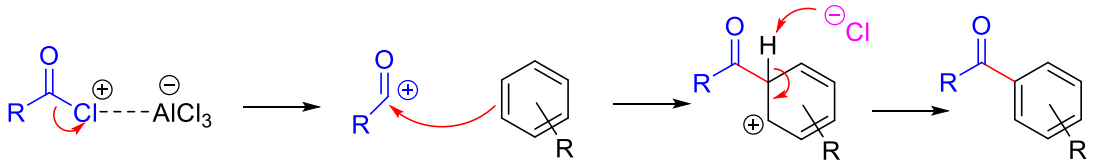


The nitration mechanism involves protonation of nitric acid followed by the loss of water to form a nitronium ion, which acts as an electrophile for the nucleophilic double bond of the arene. This momentarily breaks the aromaticity of arene, but water readily removes the acidic proton to re-establish aromaticity.

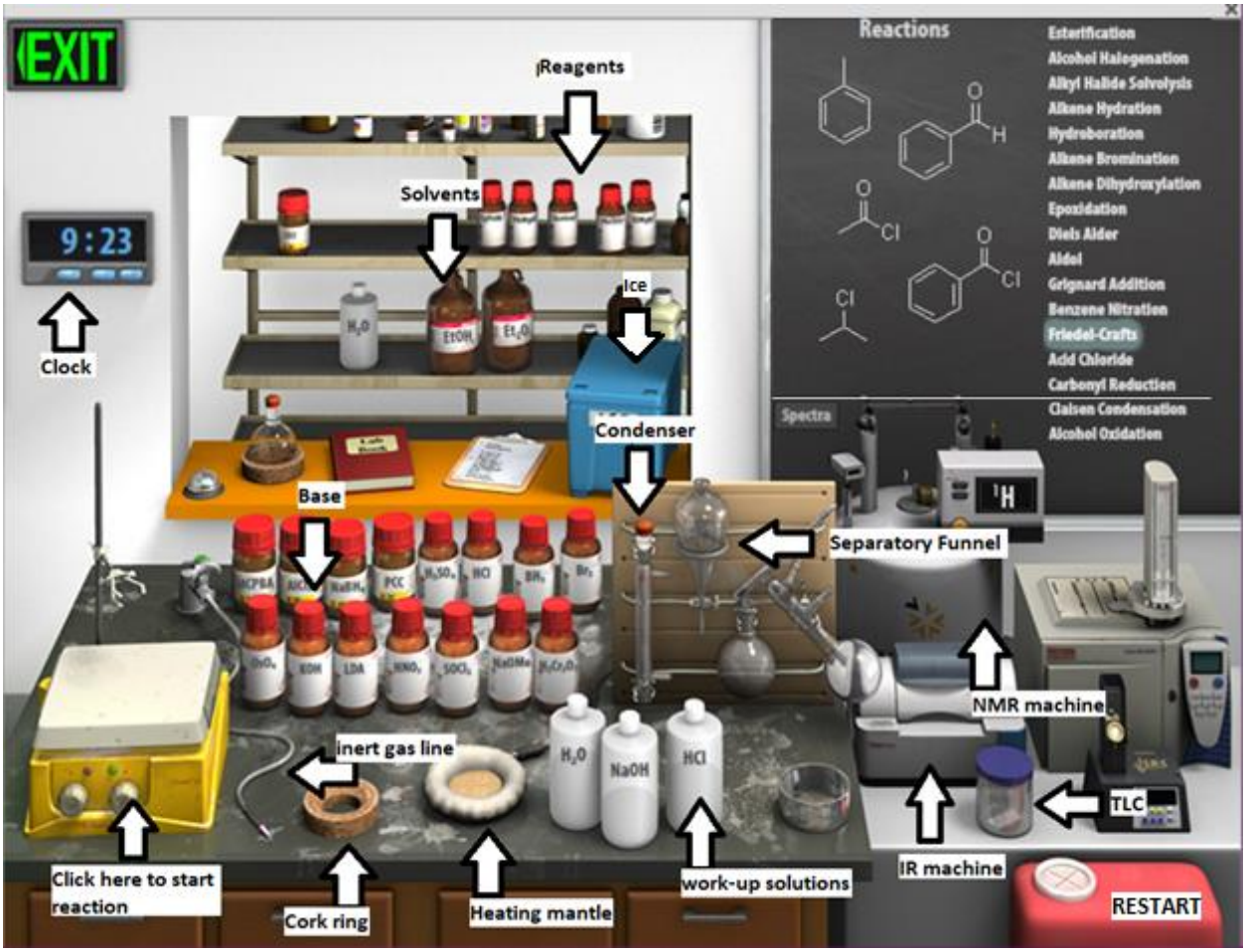




The acylation mechanism involves coordination of the acyl chloride to $AlCl_3$, a Lewis acid followed by loss of the chloride to form an acylium ion, which acts as an electrophile for the nucleophilic double bond of the arene. This momentarily breaks the aromaticity of arene, but a chloride ion readily removes the acidic proton to re-establish aromaticity.



Procedure



Part 1: Nitration

Using the BeyondLabz platform, enter the virtual organic chemistry lab. Click on the Synthesis button on the top left corner and select the Benzene Nitration reactions on the chalkboard to load the reaction specific reagents onto the stockroom shelves. Click and drag each required solvent and reagent to the round bottom flask before moving the flask to the stir plate. Add an ice bath and inert gas line before adding a nitric/sulfuric acid mixture (bottle is labelled HNO_3). Record the time (from the clock below the exit sign) and turn on the stir plate to start the reaction. You may fast forward in time by clicking on the buttons attached to the clock. Periodically check the progress of your reaction by TLC and try to stop the reaction before multiple nitrations occur. If multiple nitrations occur, you will have to restart by clicking on the chemical waste bin on the bottom left corner.

After the reaction has been completed, double click on the separatory funnel and add NaOH to work up the reaction. Drag the organic layer to the cork ring and take ^1H NMR and IR spectra of the compound by clicking on the NMR or FTIR machine and dragging it to the round bottom flask.

Part 2: Acetylation

Using the BeyondLabz platform, enter the virtual organic chemistry lab. Click on the Synthesis button on the top left corner and select the Friedel-Crafts reactions on the chalkboard to load the reaction specific reagents onto the stockroom shelves. Click and drag each required solvent and reagent to the round bottom flask before moving the flask to the stir plate. Add an inert gas line before adding $AlCl_3$. Record the time (from the clock below the exit sign) and turn on the stir plate to start the reaction. You may fast forward in time by clicking on the buttons attached to the clock. You may periodically check the progress of your reaction by TLC.

After the reaction has been completed, double click on the separatory funnel and add NaOH to work up the reaction. Drag the organic layer to the cork ring and take ^1H NMR and IR spectra of the compound by clicking on the NMR or FTIR machine and dragging it to the round bottom flask.

Discussion

Attach the ^1H NMR and IR spectra of the three compounds you virtually synthesized and label all relevant peaks.

If you have a mixture of compounds for some reactions, estimate the ratio of the products (you will not be able to identify which is the major compound yet).

Questions

Why is it difficult to get triple nitrations of toluene to get to tri-nitro-toluene (TNT)?

What kind of directing group is on toluene? Explain how this works.

What kind of directing group is on benzaldehyde? Explain how this works.