Nitration of Bromobenzene by Electrophilic Aromatic Substitution

Part A, p. 515: Nitration procedure. (p. 504, 4th Ed)
Part B, p. 517: TLC. (p. 506, 4th Ed)
Part C, p. 518: Column chromatography. (p. 507 4th Ed)

Important Concepts

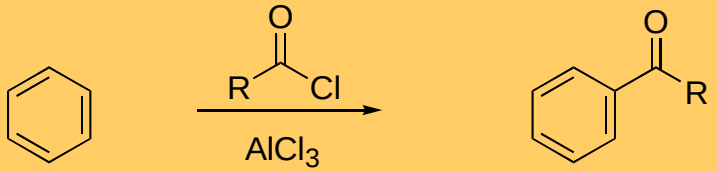
- Electrophilic aromatic substitution reactions
- Nitronium ion as an electrophile
- Activating vs Deactivating groups
- o,p-directors vs meta directors
- Using resonance structures to predict substitution pattern

Introduction to Electrophilic Aromatic Substitution

1. Friedel-Crafts Alkylation

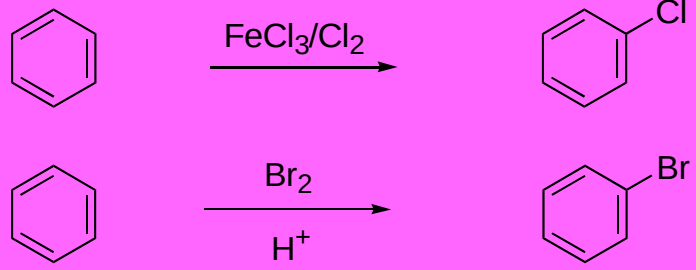
R = alkyl; X = Cl,Br, Catalyst = $AlCl_3$, etc.

2. Friedel-Crafts Acylation

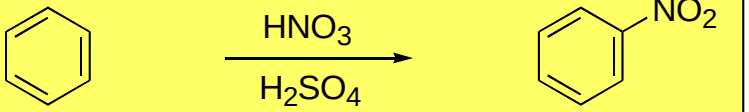


R = alkyl, aryl

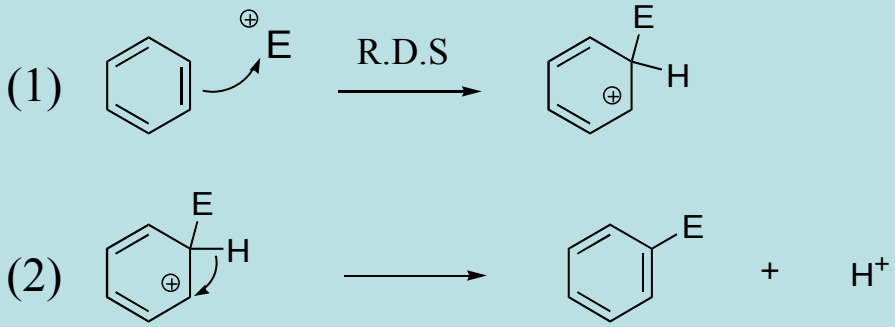
3. Halogenation



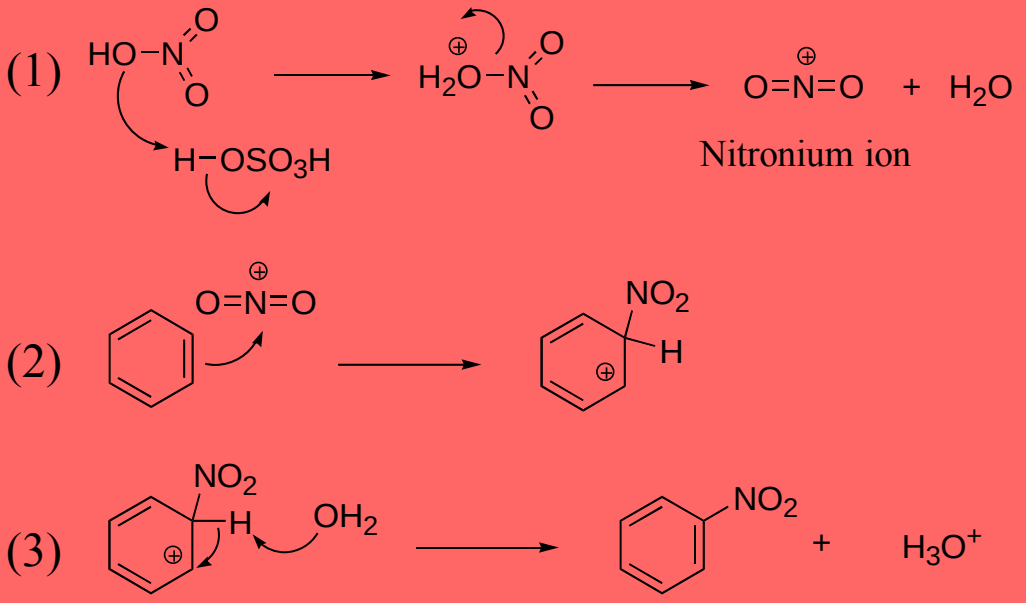
4. Nitration



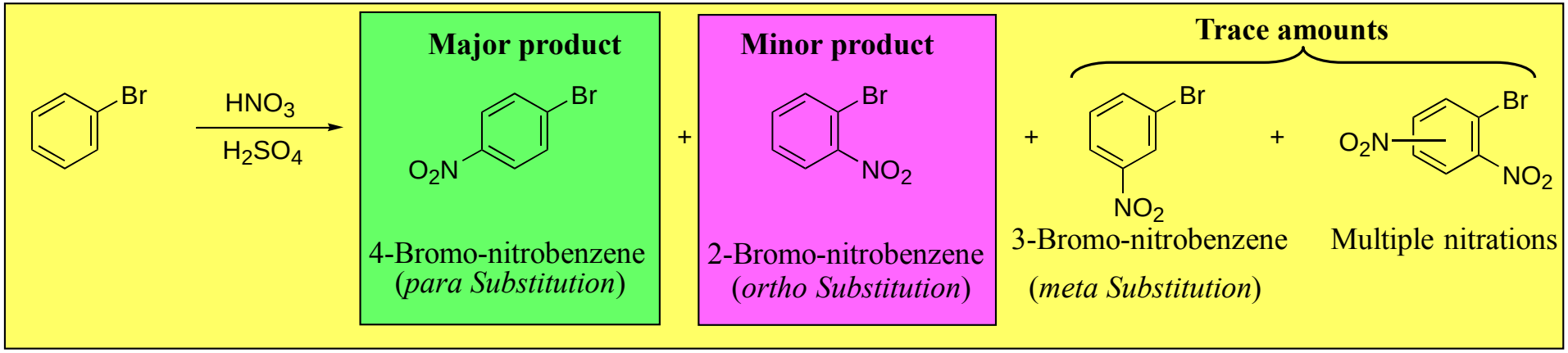
General Reaction Mechanism



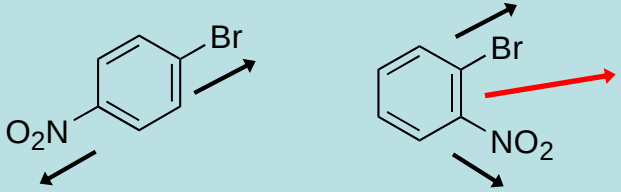
Nitration Mechanism



Our Reaction



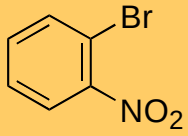
Which is more polar?



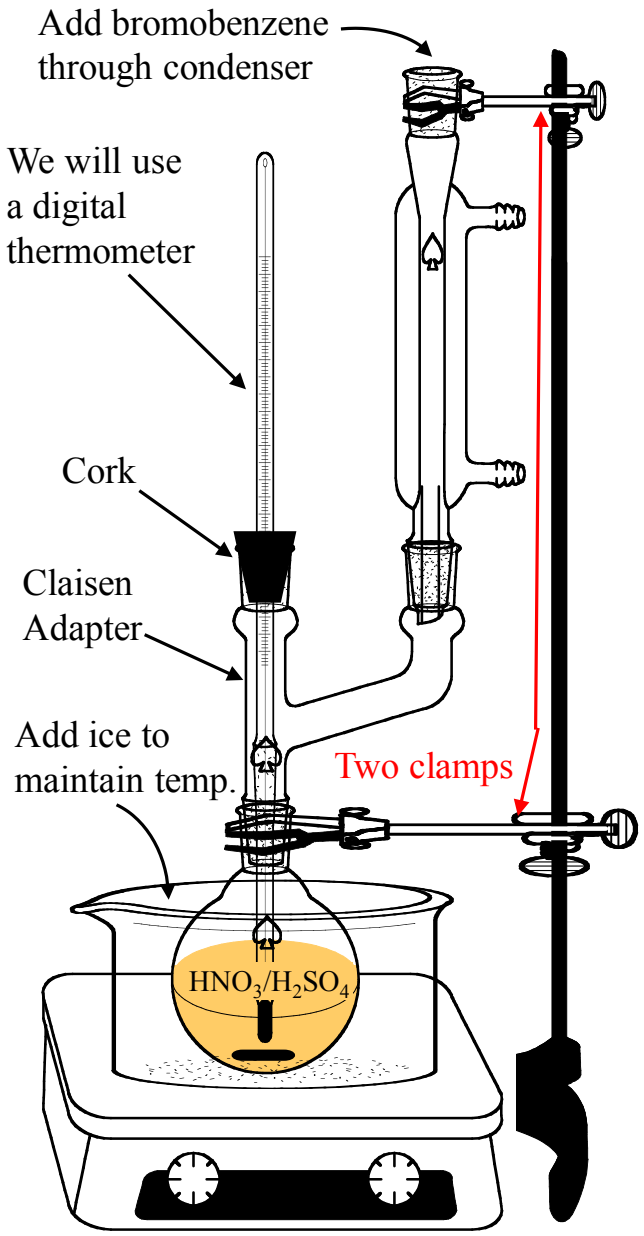
Less polar

More polar

Which product has the smallest R_F value?



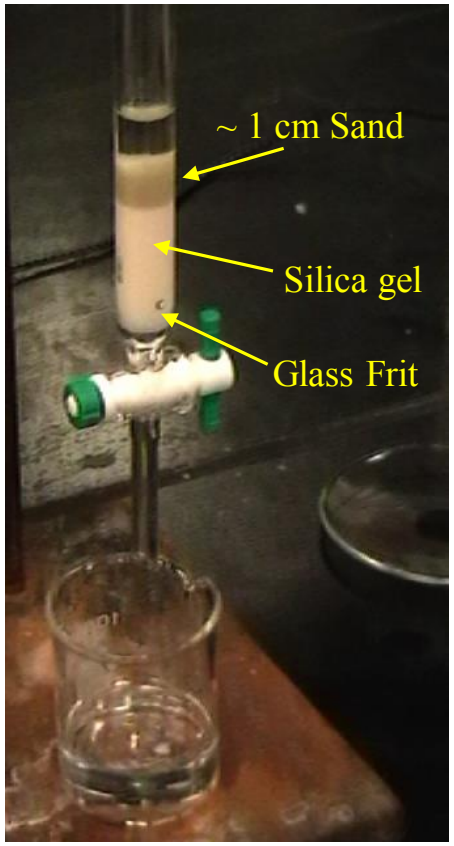
Part A - Nitration Procedure



1. Assemble apparatus as described. We will essentially follow the procedure in the book.
2. Control the rate of addition and add ice to water bath in order to keep temperature below 55 ^oC.
3. After addition, heat the solution for 15 minutes (keep temp. below 60 ^oC), then let cool to room temperature.
4. Pour into ice water and recrystallize the crude solid from 95% ethanol.
5. Concentrate the mother liquor to a slurry on the rotovap. Do not evaporate to dryness.
6. Filter the slurry from the rotovap and rinse the crystals before drying. Do not combine with the 1st crop of crystals until you have confirmed purity by TLC.
7. Concentrate mother liquor prior to column chromatography.

Part C - Column Chromatography

Use wet pack (slurry) method

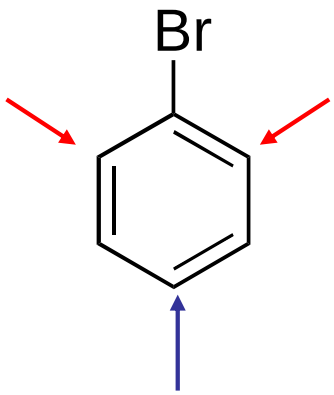


Which compound will come off the column first?

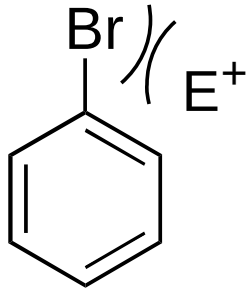
1. Fill column 25% with solvent (95/5 - Hex/EtOAc).
2. Let a little solvent flow through the frit and stopcock.
3. Place silica in beaker and add solvent, stir and swirl vigorously while you pour it into the column. Use more solvent to transfer as much silica as needed. Rinse sides of column with solvent to ensure all silica is immersed below the solvent level.
4. Fill the column with solvent and let solvent flow through column until the silica is packed tightly. Make sure that the solvent does not reach the level of the silica. It is OK to re-use the solvent that is in the collection beaker while packing the column.
5. After the column is packed tightly, add ~ 1 cm of sand above the silica gel.
6. Allow solvent to drain until it reaches the level of the sand, then load the column with your crude sample.
7. Allow a small amount of solvent to flow through the sand until you are confident that your compound has been transferred to the silica layer. Then fill the column with eluant and open the stopcock so that there is a moderate flow of solvent.

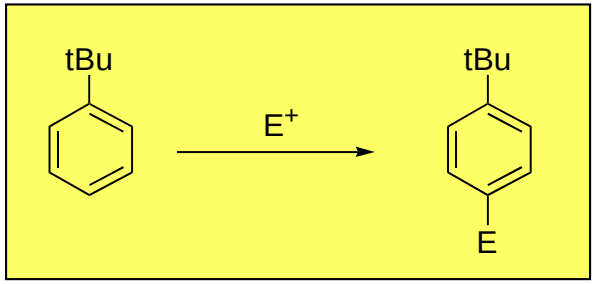
Start eluting with 95/5 and ramp up to 90/10 - Hex/EtOAc)

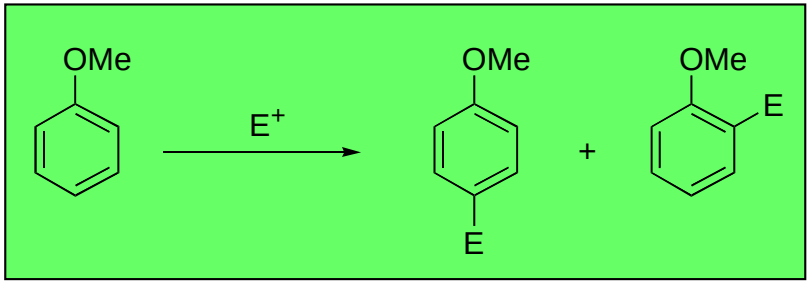
Why do we get more para than ortho? (but if any organic chemist ask in lecture for product to reaction MUST give both ortho and para products)

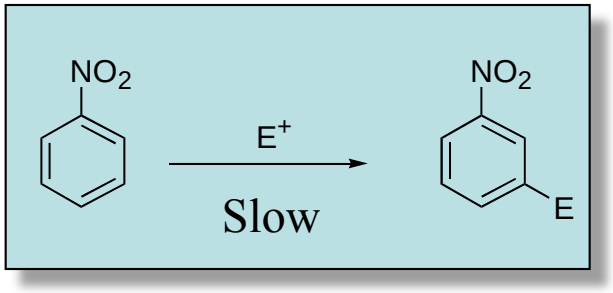


Predicted			**Observed**		
ortho		para	ortho		para
2	:	1	1	:	2









Required Data

- m.p. of purified products.

- TLC with crude, pure para and pure ortho on same plate.

- Yield, %Yield for each product.

- IR and ^{1}H NMR of organic starting materials and final products.