Experiment 37

Nucleophilic Aromatic Substitution: Microwave-Assisted Chemistry

Study Questions

1) The solvent for the reactions with ethylamine or aniline is ethanol, but the solvent for the reaction with potassium thiocyanate is a mixture of water and ethanol. Why would neither pure ethanol nor pure water work very well as the solvent for the potassium thiocyanate reaction? **Answer:** Pure ethanol will not work because potassium thiocyanate is not very soluble in it, being an ionic solid. Pure water will not work because it is less efficient at absorbing microwaves, and if this reaction were run at the same time as the two ethanol-containing reactions then it would probably not heat up as much.

2) If you were to place two reaction vessels in the microwave reactor, one filled with pure deionized water and one filled with salt water, which would heat up faster, and why? **Answer:** The salt water would heat up faster because it is being heated by both dipolar polarization and ionic conduction. The deionized water is being heated only by dipolar polarization.

3) What would happen if you were to rinse the composite sleeve for your reaction vessel with water immediately before running it in the microwave reactor? **Answer:** Since water absorbs microwaves (it is a medium-absorbing solvent), the water would heat up. Depending on how quickly this happened, it might damage the composite sleeve or reaction vessel, or only release water vapor into the reactor. It would also block some of the microwaves from reaching the contents of the reaction vessel.

4) During S_NAr reactions, electron-withdrawing groups help stabilize the charge only when they’re ortho or para to the leaving group, but not meta. Explain why this is by showing the relevant resonance structures. **Answer:** Compounds with EWGs in the ortho or para position can move the negative charge out onto the EWG itself, creating a structure with no negative charges on carbon. This is not possible for the meta compound.
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Para nitro

Ortho nitro

Meta nitro