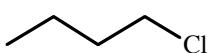
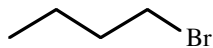


**Chem 355-Jasperse****STRUCTURAL EFFECTS ON SUBSTITUTION REACTIONS**

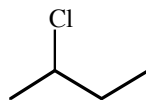
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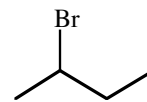
1-chlorobutane

**1**

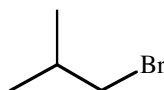
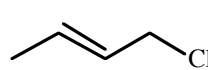
1-bromobutane

**2**

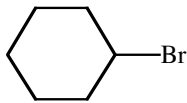
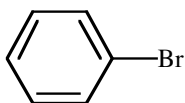
2-chlorobutane

**3**

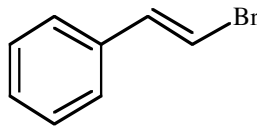
2-bromobutane

**4**2-chloro-  
2-methylpropane**5**2-bromo-  
2-methylpropane**6**1-bromo-  
2-methylpropane**7**

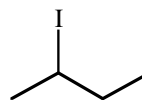
1-chloro-2-butene

**8**bromo-  
cyclohexane**9**

bromobenzene

**10**

β-Bromostyrene

**11**

2-iodobutane

**12**

General Procedure: In each test, add 5 drops of haloalkane to a test-tube, then add 1 mL of solution (NaI/acetone for the S<sub>N</sub>2 reactions, AgNO<sub>3</sub>/ethanol for the S<sub>N</sub>1 reactions), and mix by stirring vigorously with a boiling stick, and watch for the formation of precipitate. (For NaI reactions, sometimes an initial false precipitate forms and persists, that clears away if you mix it up well at the start.) For the NaI experiments, if neither of them react within 3 minutes, then place the tubes in a 50° water bath (use 50-mL beaker); allow to stand until at least one of them gives precipitate. Do not allow the bath temperature to exceed 60° or the acetone may evaporate away and you'll get false results.

What is happening, and what are the precipitates? In the NaI experiments, substitution by iodide generates either insoluble NaCl or NaBr. In the second set of experiments insoluble AgCl or AgBr are reaction products as the halide is substituted by an ethoxy group. Thus, in both types of reaction the formation of precipitate gives a qualitative and visible measurement of relative reaction speed.

For the S<sub>N</sub>2 reaction (Part 1), you'll need samples 1, 2, 3, 4, 7, 8, 10, 11. For the S<sub>N</sub>1 reaction (Part 2), you'll use all samples except for 7 and 11.

**Notes**

1. Crotyl chloride **8** is a lachrymator (makes you cry). Do not spill it, keep it the hood as much as possible, and when you rinse it out do so in the hood!
2. You are using so many test tubes that you will need to wash them between sets of experiments. Make sure that they are washed very carefully, with water and then acetone, before reusing. If there is residual haloalkane in a tube, it can really mess up your results and give you false positives. If there is water in your test tubes, it will dissolve NaCl/NaBr salts and give you false negative data.
3. In part 1, the NaI/acetone should be added last. Otherwise you get false precipitate when relatively non-polar haloalkane can cause some of the NaI to precipitate. NaI precipitate should dissolve upon mixing/shaking.
4. In NaI reactions, often yellow color will develop. This means nothing. Iodide is air-oxidized to yellow iodine, but this has no pertinence to the experiment.
5. Silver nitrate spills give brown spots! Avoid spilling. A spot on your fingernail will last till your nail grows out! (And on your clothes, forever?).

### Some Arrow-Pushing Guidelines

1. Arrows follow electron movement.
2. Some rules for the appearance of arrows
  - The arrow must begin from the electron source. There are two sources:
    - a. An atom (which must have a lone pair to give)
    - b. A bond pair (an old bond that breaks)
  - An arrow must always point directly to an atom, because when electrons move, they always go to some new atom.
3. Ignore any Spectator Atoms. Any metal atom is always a “spectator”
  - When you have a metal spectator atom, realize that the non-metal next to it must have negative charge
4. Draw all H's on any Atom Whose Bonding Changes
5. Draw all lone-pairs on any Atom whose bonding changes
6. **KEY ON BOND CHANGES**. Any two-electron bond that changes (either made or broken) must have an arrow to illustrate:
  - where it came from (new bond made) or
  - an arrow showing where it goes to (old bond broken)
7. **Watch for Formal Charges and Changes in Formal Charge**
  - If an atom's charge gets more positive => it's donating/losing an electron pair => arrow must emanate from that atom or one of its associated bonds. There are two “more positive” transactions:
    - When an anion becomes neutral. In this case, an arrow will emanate from the atom. The atom has donated a lone pair which becomes a bond pair.
    - When a neutral atom becomes cationic. In this case, the atom will be losing a bond pair, so the arrow should emanate from the bond rather than from the atom.
  - If an atom's charge gets more negative => it's accepting an electron pair => an arrow must point to that atom. Ordinarily the arrow will have started from a bond and will point to the atom.
8. **When bonds change, but Formal Charge Doesn't Change, A “Substitution” is Involved**
  - Often an atom gives up an old bond and replaces it with a new bond. This is “substitution”.
  - In this case, there will be an incoming arrow pointing directly at the atom (to illustrate formation of the new bond), and an outgoing arrow emanating from the old bond that breaks

**Chem 355-Jasperse**

Name:

**STRUCTURAL EFFECTS ON SUBSTITUTION REACTIONS**Part 1: The S<sub>N</sub>2 Reaction (NaI/acetone)

Report your observations, based on how fast precipitate formation is observed. Do you get instant precipitation? Does it take minutes for much precipitate to build up? Do you need to heat in order to get much precipitate? After comparing, rank the relative reactivity of the competing substrates.

1. Leaving Group: Br vs Cl

Run 1 vs 2

Run 3 vs 4

2. Primary/Secondary/Tertiary: (With tertiary, results in these reactions are confusing due to competing side reactions, so we aren't actually racing.)

Run 2 vs 4

Run 1 vs 3

3. Double bonds part 1: Alkyl vs. Allylic

Run 1 vs 8

4. Compare 2 vs 8. This is an apples/oranges comparison; which is more important, the leaving group or the allylic double bond effect?

Run 2 vs 8

5. Double bonds part 2: Alkyl vs. Alkenyl ("vinyl") or Aryl. (Stir with boiling sticks for 10 and 11. Look for just one winner, neither of two losers should react at all).

Run 2 vs 11 vs 10

6. Steric effects: Both 2 and 7 are both primary. Are they equal, and if not why not?

Run 2 vs 7

7. Temperature. Did heating samples sometimes lead to reactions that didn't go at room temperature?

Part 2: The S<sub>N</sub>1 Reaction (AgNO<sub>3</sub>/ethanol)

1. Leaving Group: I vs. Br vs Cl (Record 1<sup>st</sup>/2<sup>nd</sup>/3<sup>rd</sup> places)

Run 12 vs 3 vs 4

2. Primary/Secondary/Tertiary: (Record 1<sup>st</sup>/2<sup>nd</sup>/3<sup>rd</sup> places)

Run 1 vs 3 vs 5

Run 2 vs 4 vs 6

3. Double bonds part 1: Alkyl vs. Allylic:

Run 1 vs 8

4. Double bonds part 2: Alkyl vs. Alkenyl ("vinyl")/Aryl.

Run 9 vs 10

Name:

**STRUCTURAL EFFECTS ON SUBSTITUTION REACTIONS**

1. When considering the leaving groups I, Br or Cl, what was the relative reactivity in S<sub>N</sub>1 reactions? In S<sub>N</sub>2 reactions (didn't actually use the iodide there)?
2. When considering primary versus secondary versus tertiary haloalkanes, what was the relative reactivity toward S<sub>N</sub>1 reactions? Toward S<sub>N</sub>2 reactions (we didn't actually run a tertiary there)?
3. What was the effect of the "allylic" double bond in **8** on S<sub>N</sub>1 reactivity? On S<sub>N</sub>2 reactivity?
4. What was the effect of the halide being directly attached to an aryl/alkenyl carbon (**10** and **11**) on the S<sub>N</sub>2 reactivity? S<sub>N</sub>1 reactivity?
5. Both **2** and **7** are primary bromides. Can you explain the difference in their S<sub>N</sub>2 reactivity, if there was any?
6. What would be the specific mathematical effect on the reaction rate if you carried out the sodium iodide-in-acetone reactions on the alkyl halides using an iodide solution half as concentrated? ("Slower" or "faster" is not specific enough.)

Name:

## Arrow-Pushing Practice:

- Draw arrows for each of the steps in the following reactions.
- Include all formal charges, where present.
- Include all lone-pairs on atoms that react.
- Draw in all hydrogens on atoms that react. (It is not useful to draw in all H's on atoms that don't react.)
- Remember that arrows track the movement of electrons, so an arrow should go from the source of electrons and point directly to the atom that accepts them.

