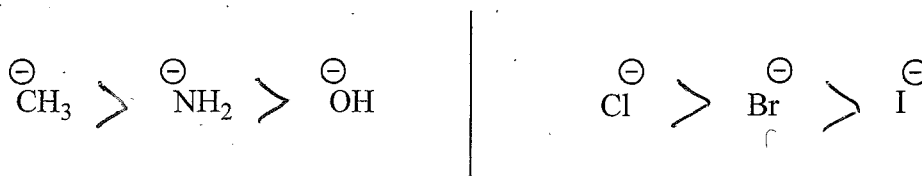


Chem 51A – SSI 2014
Discussion 8 Worksheet
Dr. Renee Link

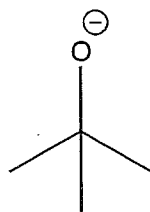
This worksheet will focus on concepts to be discussed or already discussed, in Chapter 7. Those concepts being 1) Alkyl halides and 2) Nucleophilic Substitution Reactions.

There are many aspects that determine a nucleophile's strength. In each sequence of compounds below, rate as increasing to decreasing in nucleophile strength.



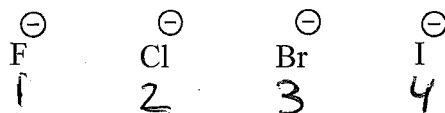
In the above cases, the order is based upon the basicity of the compound, with stronger bases being stronger nucleophiles.

The below compound is a strong base, but is a poor nucleophile. Why?



The oxygen is sterically crowded by the three methyl groups.

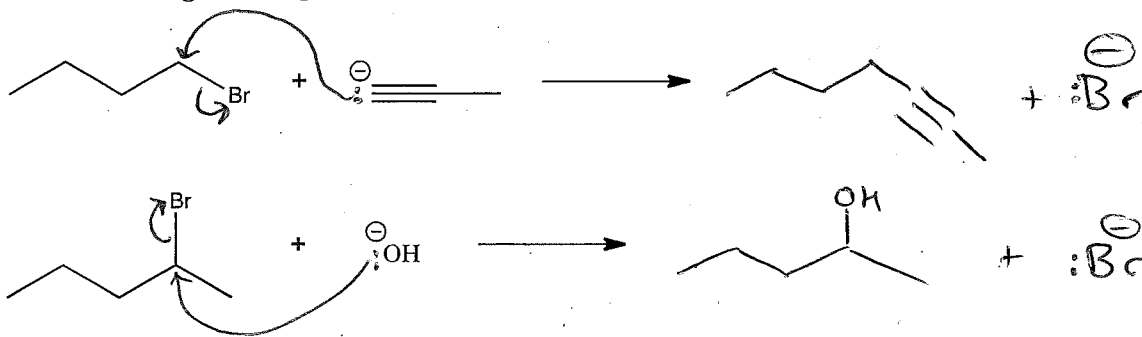
The final consideration of nucleophile strength is solvent type. Polar solvents can be either **protic** or **aprotic**. You must be able to classify a solvent when presented with one. **Polar protic** solvents strongly solvate, or trap, anions. Rate the below anions 1-4 in terms of easiest to hardest to trap, with 1 being the easiest.



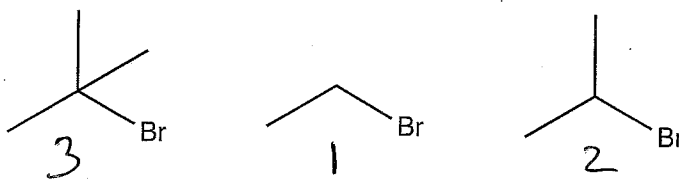
Polar aprotic solvents do not trap anions well. As a result, polar aprotic solvents do not affect nucleophile strength much. If that is true, what do you look at to determine nucleophile strength in a polar aprotic solvent?

Stability of the negative charge.

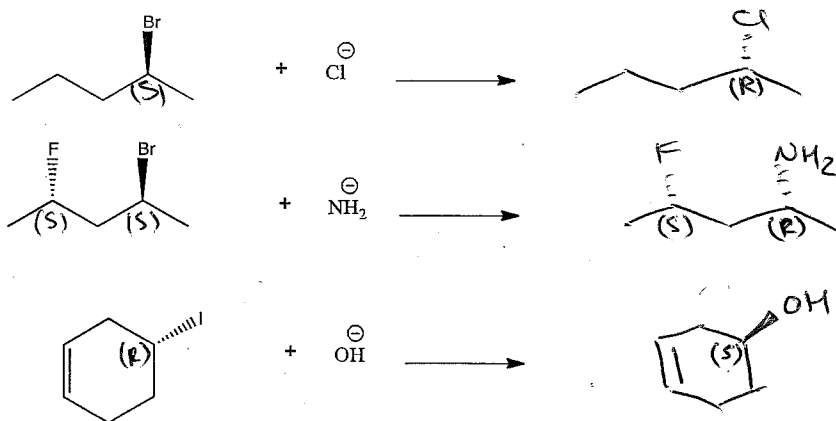
The S_N2 mechanism of a nucleophilic substitution reaction is a **concerted**, **bimolecular** process. Draw the mechanism and the products of the two reactions below, using an S_N2 process.



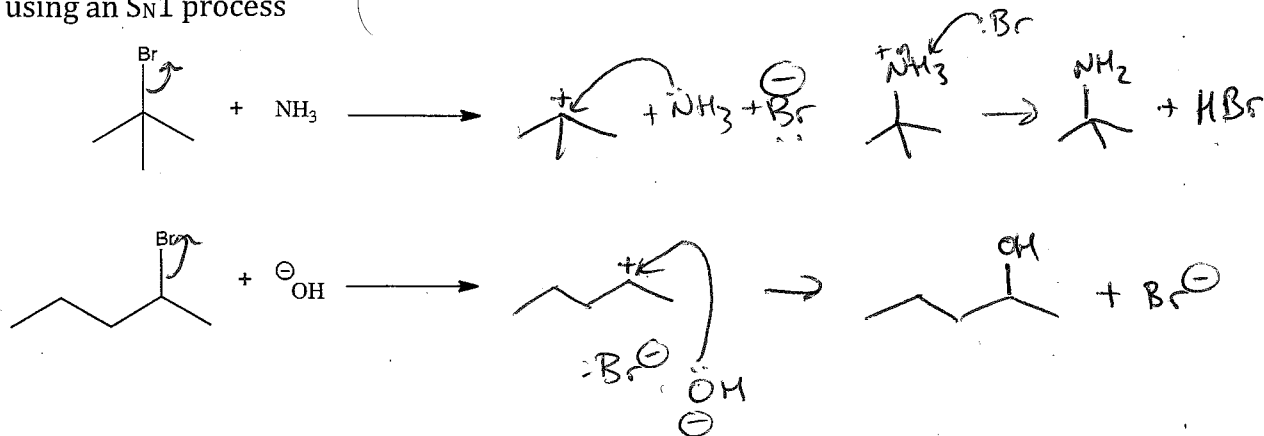
Knowing that, rate the below compounds 1-3 based on how fast they undergo S_N2 reactions, with 1 being the fastest.



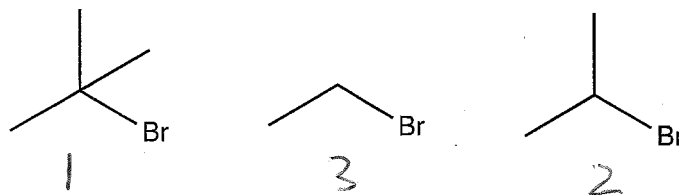
Another consequence of this backside attack is related to stereochemistry. In each of the reactions below, draw the product with the correct stereochemistry. Assign R and S to each stereocenter in the starting materials and the products.



The S_N1 mechanism is a **stepwise** process that goes through a **carbocation intermediate**. Draw the mechanism and the products of the two reactions below, using an S_N1 process



The carbocation is a particularly high-energy reactive intermediate. It can exist only when stabilized by a sufficient number of adjacent carbons. Rate the below compounds 1-3 based on how fast they undergo S_N1 reactions, with 1 being the fastest.



What is the electron geometry of the carbocation intermediate?

trigonal planar

From what directions can a nucleophile attack a carbocation intermediate?

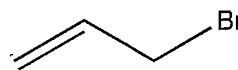
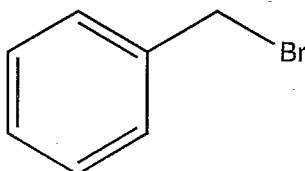
top or bottom

If you start with a compound that is enantiopure at one stereocenter, what happens to that stereocenter if it is involved in an S_N1 mechanism?

It racemizes

Challenge questions for home

The below structures are not considered primary alkyl halides and can undergo S_N1 mechanism substitution. Why? Drawing structures may help.



Both of these structures can form resonance-stabilized cations.