Experiment #6

Nucleophilic Substitution of Alkyl Halides

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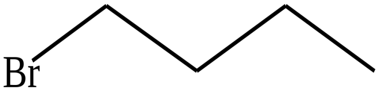
Date Performed--October 26, 2020
Date Due--October 27, 2020

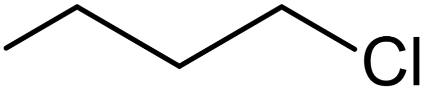
Experimental Objective

To understand and predict the products of a substitution reaction and the SN^1 and SN^2 reaction mechanisms under various conditions.

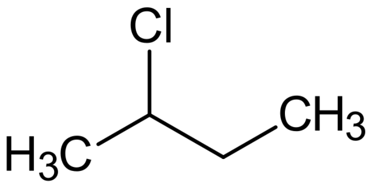
Reagents Used



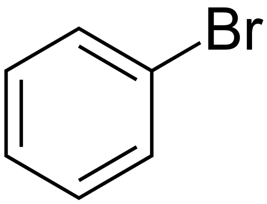
1-bromobutane



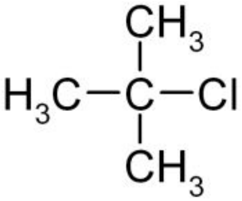
1-chlorobutane



2-chlorobutane

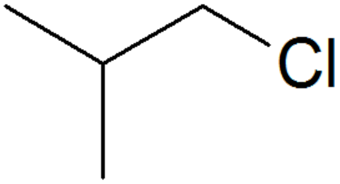


bromobenzene



$$H_3C-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-Cl$$

2-chloro-2-methylpropane



1-chloro-2-methylpropane

$AgNO_3$ / EtOH

NaI / acetone

Reaction Scheme

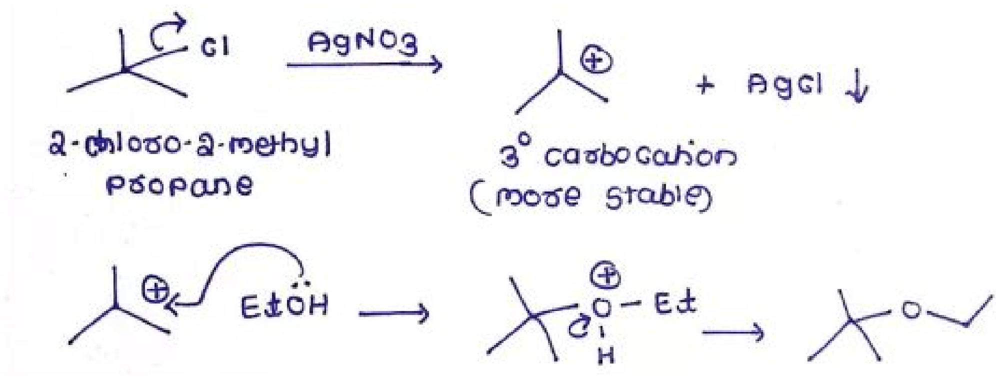


Figure 1. Example of $AgNO_3$ / EtOH SN^1 Mechanism (generation of a 3° carbocation)

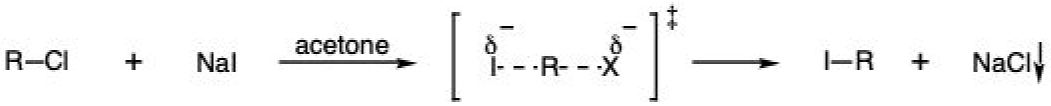


Figure 2. Example of NaI / acetone SN^2 Mechanism (strong Nucleophile, polar aprotic solvent)

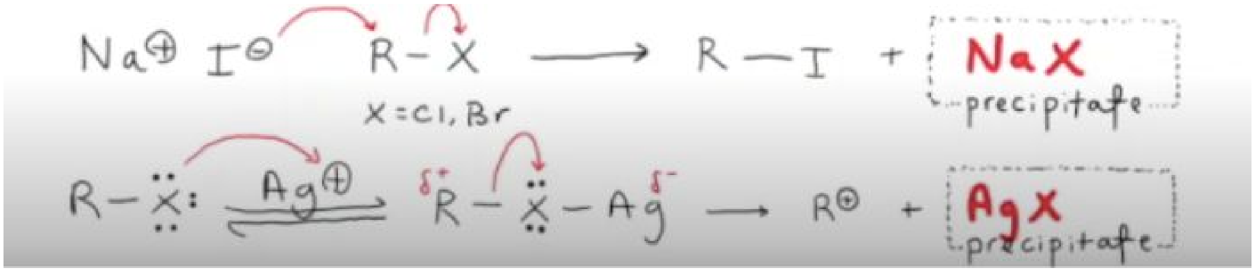


Figure 3. Mechanisms of this Nucleophilic Substitution lab

Procedure

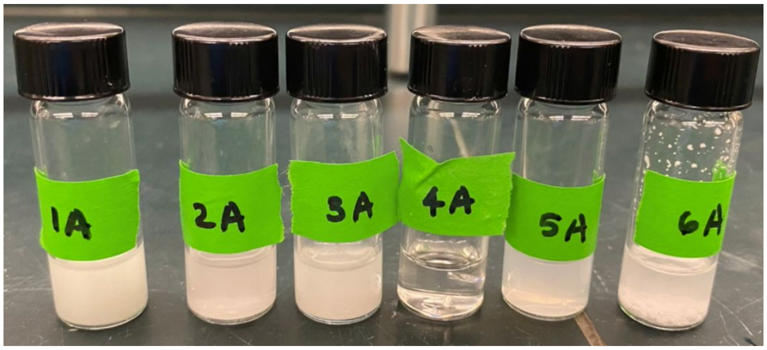
Silver nitrate in EtOH (1%)

Six 0.3mL vials are obtained and with a syringe and a sharp needle ~0.1mL each of the six respective alkyl halides is added to the vial, sealing and labeling the cap after each addition. Next, a graduated pipette and pipette pump is used to add ~1.0mL of the silver nitrate in EtOH (1%) to each of the six vials, again sealing the lids after the addition to prevent air and solvent exposure. The observation of a precipitate is demonstrative of the reaction occurring; however, because the six alkyl halides may not react immediately, some may require aggravation or heating in order to react. In the case of heating, a 50mL beaker is filled halfway with water and the unreacted vials are heated to 50℃ (conservative temperature due to the implicit danger in heating a closed system) or Level 1 until a precipitate forms or 5 minutes passes. The physical product description and reaction-time observations are noted. Once your vials are capped, do not open them again. Dispose of the whole vial in the proper waste container.

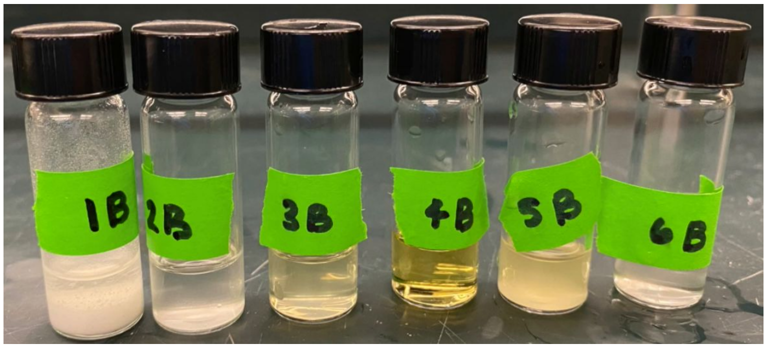
Sodium iodide in acetone (18%)

Six 0.3mL vials are obtained and with a syringe and a sharp needle ~0.1mL each of the six respective alkyl halides is added to the vial, sealing and labeling the cap after each addition. Next, a graduated pipette and pipette pump is used to add ~1.0mL of the sodium iodide in acetone (18%) to each of the six vials, again sealing the lids after the addition to prevent air and solvent exposure. The observation of a precipitate is demonstrative of the reaction occurring; however, because the six alkyl halides may not react immediately, some may require aggravation or heating in order to react. In the case of heating, a 50mL beaker is filled halfway with water and the unreacted vials are heated to 50℃ (conservative temperature due to the implicit danger in heating a closed system) or Level 1 until a precipitate forms or 5 minutes passes. The physical product description and reaction-time observations are noted. Once your vials are capped, do not open them again. Dispose of the whole vial in the proper waste container.

Results



Silver nitrate in EtOH (1%)



Sodium iodide in acetone (18%)

Solvent System	**SN1 or SN2? Explain, taking into account the nucleophile type and solvent type.**
Silver nitrate in EtOH (1%)	SN^1 Mechanism (generation of a 3° carbocation). Ethanol is a polar protic solvent, and a poor nucleophile. The silver ion coordinates with the halide ion in the alkyl halide and enhances carbocation formation.
Sodium iodide in acetone (18%)	Iodide ion is a strong nucleophile, and SN^2 reactions are favored in polar aprotic solvents such as acetone.

Silver nitrate in EtOH (1%)	**Compound ID**	**Predicted Reaction Outcome**	**Justification for Predicted Reaction Outcome**	**Observed Reaction Speed**	**Physical Description of Product**	**Expected?**
#1	1-bromobutane	Yes	1°	Immediate	Cloudy liquid,	Yes

					some crystal-like features	
#2	1-chlorobutane	Yes	1°	Yes	Cloudy	Yes
#3	2-chlorobutane	No	2°	After heating	Cloudy	No
#4	bromobenzene	No	structure of the ring (does not allow for formation of a carbocation)	No	Clear liquid	Yes
#5	1-chloro 2-methylpropane	No	1°	Agitated	Cloudy	No
#6	2-chloro 2-methylpropane	Yes	3°	Immediate	Cloudy	Yes

Sodium iodide in acetone (18%)	**Compound ID**	**Predicted Reaction Outcome**	**Justification for Predicted Reaction Outcome**	**Observed Reaction**	**Physical Description of Product**	**Expected?**
#1	1-bromobutane	Yes	1°	Immediate	Cloudy, dense/thick -looking	Yes
#2	1-chlorobutane	Yes	1°	Agitated	Clear/cloudy/ murky	Yes
#3	2-chlorobutane	Yes	2°	After heating	Slightly yellow and murky	Yes
#4	bromobenzene	No	structure of the ring (does not allow for backside	No	Color change, yellowish tone	Yes

			attack)			
#5	1-chloro 2-methylpropane	No	1° (hindered)	After heating	Color change, yellow and murky	Yes
#6	2-chloro 2-methylpropane	No	3°	No	Clear liquid	Yes

Conclusion

Overall the purpose of this experiment is to demonstrate nucleophilic substitution reactions, SN^1 ($AgNO_3$ in ethanol) and SN^2 (NaI in acetone) with the addition of a solvent to mixtures of alkyl halides in a hands-on, laboratory setting. In order to ensure the effectiveness and precision of the single trial, observations were noted while each reaction occurred. That being said, the two nucleophilic substitution mechanisms differ as the SN^2 reaction involves a one step concerted displacement of the leaving group by a nucleophile with inversion of configuration (weak bases are more stable, and therefore make for better leaving groups); however, the SN^1 reaction is a 2-step reaction involving loss of the leaving group to form a carbocation intermediate, followed by attack by a weak nucleophile with loss of stereochemistry (SN^2 reaction is suppressed because of the absence of a good nucleophile). That is to say, four aspects determine whether a SN^1 or SN^2 path will be taken: structure of the electrophile, nucleophile strength, leaving group ability, and solvent type. A tertiary electrophile and a protic solvent favor SN^1 (3°> 2°> 1°> CH_3 > vinyl), while a primary electrophile, a strong nucleophile favor, and an aprotic solvent SN^2 (3°< 2°<1°< CH_3). For the SN^2 , an aprotic solvent was used (NaI in acetone), in that no hydrogen ion could be donated. For SN^1 reactions, a polar protic solvent is best for the reaction to occur, or, a solvent in which a hydrogen ion can be readily donated (as seen in ethanolic silver nitrate). Heat must be added to break the hydrogen bonds, and then the hydrogen on the ethanol can be donated, making the solvent protic again, so then the SN^1 reaction can occur for 2-chlorobutane. Consequently, it can be concluded that as with any reaction, heat helped the reaction proceed because it increased kinetic energy, or helped the molecules experience more collisions.