C321

Lab

Handouts

Fall 2010

Stereoisomerism:

In this experiment you will construct models that illustrate the concepts of chirality, chiral center (asymmetric carbon atom), enantiomers, diastereomers, and meso forms. You will also learn about two conventions, *R*–*S* and Fischer, for designating the configurations of chiral molecules.

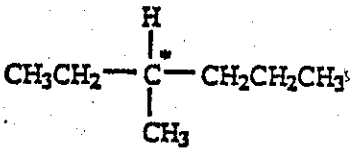
1 A Chiral Center

Procedure Construct a model* in which a tetrahedral (sp^3) carbon atom has four different colored model atoms attached to it—red, yellow, green, and black—representing four different atoms or groups attached to the central atom.

Answer all numbered questions directly on the report sheets.

1. Does the model have a plane of symmetry?
2. Does it have a center of symmetry or an axis of symmetry?

A carbon atom that has four different groups attached to it is a chiral center, or an asymmetric carbon atom. The carbon marked with an asterisk in 3-methylhexane is a chiral center.



3. What four different groups are attached to the chiral center in 3-methylhexane?

Replace the green atom (or group) in your model with a second yellow atom. Now two of the groups attached to the carbon atom are identical:

4. Does the model now have a plane of symmetry? Describe it.
5. Draw structural formulas for the following compounds, and mark any chiral centers (asymmetric carbons) with an asterisk: 1-bromobutane, 2-bromobutane, 1,2-dibromobutane, 1,3-dibromobutane, 1,4-dibromobutane, 2,3-dibromobutane.

2 Chirality and Enantiomers

A center of chirality (from the Greek *cheir*, hand) imparts the property of handedness to a molecule. In this part of the experiment, the left- or right-handedness of molecules with a chiral center will be illustrated with models.

A molecule is said to be chiral (that is, to have the property of handedness) if its mirror image is *not* identical to it. The mirror image of a left hand, for example, is a *right* hand. A molecule that is achiral has a mirror image that is identical to it. We shall see that any molecule with a plane of symmetry or a center of symmetry is achiral.

Procedure Reconstruct the original model (carbon with red, yellow, green, and black atoms attached). Set the model on the desk top so that the substituent black atom points toward the ceiling.

6. Looking down on the model and proceeding *clockwise* from the green atom, record the colors of the three atoms that rest on the desk top.

Now construct a second model that is the mirror image of the first, and place it on the desk top with the black atom up:

7. In which direction, clockwise or counterclockwise, must you proceed in order to list the *same* sequence of colors of the three atoms resting on the desk's surface?

Try to superimpose the two models.

8. How do the models differ from one another?

The two models that you have just constructed represent chiral molecules—they lack a plane of symmetry or center of symmetry and have mirror images that are *not* superimposable. Two substances the molecular structures of which are related as an object and its nonsuperimposable mirror image are called **enantiomers**. They differ from each other *only* in properties that have a direction or "handedness," such as, for example, the *direction* (clockwise or counterclockwise) in which they rotate a beam of plane-polarized light. Because of this latter property, such substances are sometimes called **optical isomers**. They are **optically active**.

Now we will examine the consequence of having at least two *identical* atoms or groups attached to a tetrahedral carbon atom.

Replace the green atom in each model with a yellow atom, so that each model has two identical groups attached to the central carbon atom:

9. Are the models still mirror images?
10. Does either of the models have a plane of symmetry? Where?
11. Are the models superimposable?
12. Do the models represent identical molecules or different molecules?

Place each model on the desk so that the black substituent points up.

13. To define the same sequence of colors for the three atoms resting on the desk top, must you proceed clockwise or counterclockwise?
14. Are the models chiral (handed)?

The models you have just studied represent **achiral molecules**. Their mirror images are identical to them. They are **optically inactive**. Any molecule that has a plane of symmetry or a center of symmetry is achiral.

3 Diastereomers and Meso Forms

For any molecule that has two or more chiral centers, it is possible to have stereoisomers that are not mirror images. Stereoisomers that are not related as enantiomers are called **diastereomers**. Diastereomers differ in *all* properties, chiral and achiral.

Procedure Construct a model with four different groups (black, yellow, red, and green) attached to a central carbon atom (black). Construct another model *identical* to the first. (Be sure they are identical by making sure the models are superimposable.) Now remove the black substituent from each model and connect the two carbon atoms with a bond.

15. How many chiral centers (asymmetric carbons) does this model have?
16. What four different groups are attached to each chiral center? (Note that each chiral center has the same four groups attached.)
17. Does the model have a plane of symmetry or a center of symmetry in any of its conformations?

Construct the mirror image of the first model.

18. Is the mirror image identical to or different from the first model?
19. What term describes the two models?
20. Is each model chiral or achiral?

Now interchange a green and yellow atom on the *same* carbon in *one* of the models.

21. Are the models identical or different now?
22. Are they mirror images (enantiomers)?
23. Are they stereoisomers?
24. What term describes the two models?

Carefully examine the conformations of the model in which you interchanged the green and yellow atoms.

25. Does the model have a conformation with a plane of symmetry? If so, draw that conformation and locate the plane.
26. ~~Does the model have a conformation with a center of symmetry? If so, draw that conformation and locate the center of symmetry.~~
27. Would the mirror image of this model be identical (superimposable) or different from the model itself? Verify your prediction by constructing the mirror-image model.
28. Is this model chiral or achiral?
29. Would a molecule corresponding to this model be optically active?

The last model studied here represents a meso form. The model possesses two chiral centers, but they are of *equal* and *opposite* chirality. This situation arises when a molecule has two *identical* chiral centers. Because the molecule has a readily accessible conformation with a plane of symmetry, it is achiral and optically inactive.

Tartaric acid is a molecule that corresponds to the models constructed in this section of the experiment.

tartaric acid

It exists in three forms; two are optically active enantiomers, and the third is an optically inactive meso form that is a diastereomer of the optically active forms.

30. Draw Newman projection formulas (looking at the bond between C-2 and C-3) for the three tartaric acids. Label pairs of enantiomers and diastereomers, as well as the meso form.

When a molecule has two *different* chiral centers, it may exist in four optically active forms (two pairs of enantiomers). To illustrate this with the models you just used, replace one of the colored atoms on one of the carbon atoms with a black atom. There are now four distinct ways of constructing the models: two pairs of enantiomers. Verify this by constructing one pair of enantiomers yourself while your neighbor prepares the other.

31. What name is given to a pair of molecules consisting of one molecule represented by the model that you constructed and one molecule represented by the model that your neighbor constructed?

Several conventions have been devised to designate the arrangement of groups (called the **configuration**) around a chiral center. The next two sections illustrate the two most important of these conventions.

4 The *R*–*S* Convention

The letter *R* (from *rectus*, right) or *S* (from *sinister*, left) is used to designate the configuration at a chiral center. The four atoms or groups attached to the chiral center are arranged in a priority order *according to atomic number: the higher the atomic number, the higher the priority.** If two atoms have the same atomic number, we move to the next atoms out from the chiral center, or even further, until we observe a difference in atomic number. We then view the molecule from the side *opposite* the group with the lowest priority. If the remaining three groups in order from highest to lowest priority form a clockwise array, the configuration is *R*; if they form a counterclockwise array, the configuration is *S*.

Procedure Construct a model of 2-chlorobutane.

32. Which carbon in the chain is a chiral center?
33. What are the four groups attached to this chiral center?
34. Which group has the highest priority?
35. Which group has the lowest priority?
36. What is the priority order of the other two groups?

Set the model on the desk top so that it can be viewed from the side opposite the hydrogen, which is the lowest-priority group attached to the chiral center.

37. On the report sheet, fill in the remaining groups attached to the chiral center in the model you constructed. Put the chlorine atom at the top.
38. When viewed as shown above, do the three remaining groups in priority-order sequence form a clockwise or a counterclockwise array?
39. What configuration does your model have, *R* or *S* ?

Interchange *any* two groups attached to the chiral center.

40. What configuration, *R* or *S*, does the model have now?

Note that to change *configuration* we must disconnect and remake bonds, whereas we can change *conformation* by rotating groups around single bonds.

Extraction of Caffeine

For background information, see pgs. 53-54 of your lab book.

Updated Procedure

Materials and Equipment

Tea Bags	hot plate
Deoinized Water	250 mL Beaker
Sodium Carbonate	400 mL Beaker
Dichloromethane (methylene chloride)	125 mL separatory funnel/stopper
Glass Wool	125 mL Erlenmeyer flasks
Anhydrous Sodium Sulfate	funnel
Glass stirring rod	100 mL round bottom flask
Boiling stones	Rotary Evaporator
Ice Bath	Silica Plate
	TLC Developing Solution

Reagents and Properties

Substance	*Quantity*	*mol mass (g/mol)*	*bp (°C)*
Dichloromethane	50 mL	84.93	40
Deionized Water	200 mL	18.02	100
Sodium Carbonate	10 g	105.99	--

Set up a hot plate and place 200 mL deoizined water and several boiling stones in a 400 mL beaker. Heat to a vigorous boil. Meanwhile, place 5 tea bags and 10 g sodium carbonate in a 250 mL beaker. *Carefully* pour 75 mL boiling water over the tea bags and let stand for 5-7 minutes. Stir occasionally with a glass stirring rod to aid extraction and dissolution of the sodium carbonate. Decant the dark alkaline tea into a separate 125 mL Erlenmeyer flask. Pour another 25 mL boiling water over the tea bangs and let stand for another 5 minutes. Combine the second extraction with the first in the flask. With a stirring rod, squeeze any remaining liquid from the tea bags and combine with the other tea in the flask. Place the flask with the hot tea into an ice bath. ***The tea must be at room temperature before the next step.***

Set up a ring stand and a clamp with a small iron ring. Obtain a 125 mL separatory funnel with matching stopper (the stopper, glass or plastic, must give a tight seal – if you are not sure, ask your TA). Place the separatory funnel in the iron ring, making sure the ring holds the funnel. *Close the stopcock.* Pour the cold tea into the separatory funnel and then add 15 mL dichloromethane. Seal the funnel with the stopper. Using one hand to secure the stopper in place, invert the funnel and vent by opening and closing the stopcock (*do not point the funnel at anyone). Pressure can build up in a separatory funnel as*

you work, so make sure you vent often. Mix the layers by *gently* rocking the funnel back and forth as your TA showed you. It is important to intimately mix the two layers to get a good extraction, but shaking too vigorously will cause an emulsion to form. Emulsions form when small liquid droplets become dispersed in another immiscible liquid. Stable emulsions can be difficult to separate. See below on how to remove an emulsion should it form.

After mixing, place the funnel back in the ring, remove the stopper, and allow the layers to separate. This may take several minutes. If the layers separate, drain the bottom later into a clean flask making sure not to allow any of the dark tea to drain as well. Repeat the extraction twice more with 15 mL portions of dichloromethane and combine the extracts.

If An Emulsion Forms

If an emulsion forms, place a wad of glass wool into a long stem funnel in a flask. Drain the bottom layer, including the emulsion, directly into the middle of the wad of glass wool. Allow the liquid to filter by gravity; do not squeeze it through the glass wool. If done correctly, clear liquid should pass through and the dark aqueous phase should be trapped in the glass wool

To complete the drying of the dichloromethane extract, add a little anhydrous sodium sulfate to the extract and swirl. Initially, as the drying agent pulls out the residual water, the powder will form clumps. Keep adding more drying agent with swirling until new powder is free flowing and the liquid is clear (no haze). You should ask your TA how much to add if you are unclear – adding too much can cause complications. Let stand for 5 minutes

Weigh a 100 mL round bottom flask. Carefully decant the dichloromethane into the weighed container being sure to leave behind the insoluble sodium sulfate. Rinse the drying agent with 5 mL of fresh dichloromethane and decant again into the weight container. Give your round bottom flask to your TA to complete the evaporation process.

After evaporating your dichloromethane off, you should notice solid caffeine in the bottom and on the sides of your round bottom flask. Re-weigh your round bottom flask to obtain the weight of isolated caffeine. Obtain the amount of tea found in one tea bag, and calculate the % of caffeine in tea. Also, obtain the amount of caffeine found in one tea bag, and calculate the % of caffeine you extracted.

Re-dissolve your caffeine into 5 mL of dichloromethane. Obtain a spotter and lightly spot your dichloromethane/caffeine mixture on a TLC plate. In addition, spot the standard caffeine provided next to your mixture, leaving a few millimeters distance between the spots. Once spotted, place the TLC plate in clean 400 mL beaker, containiner 1 cm of the developing solution provided (it is an ethyl acetate/hexane mixture). Place a watch glass over the top of the beaker and allow the TLC plate to develop. Be careful not to forget about your TLC plate, and mark with a pencil the position of the solvent front prior to removal. Once your TLC plate has developed, remove it from the beaker and allow the solvent to quickly dry off. Place the plate under the UV light to see what UV-active compounds there are. Draw circles around any spots you see, and compare your unknown spot(s) to the known caffeine standard you co-spotted. Record any extra spots that you see.

Post Lab Questions:

1. Calculate the mass percent of caffeine in your instant tea sample.
2. On the average, people use one teaspoon (2.5 g) of instant tea to make an 8-oz glass of iced tea. The average glass of iced tea contains 10 mg of caffeine per oz.
    a. Calculate the mass percent of caffeine in a glass of iced tea.
    b. Are your experimental results consistent with these facts? Briefly explain.
    c. If not, explain why your experimental results differ from these data.
3. Compare the spots on your TLC plate. Do they match up? Are there additional products? Briefly explain.

Distilliation

For background information, see pgs. 29-35 of your lab book.

Updated Procedure

Materials and Equipment

- Aluminum Foil
- Boiling Chips
- Electric Flask Heater, with regulator
- Glassware
  - Condenser
  - Distilling Head
  - Fractionating column
  - 100 mL Round bottom flask
  - Thermometer with adapter
- Rubber Tubing
- 2 support rings
- 2 support stands
- 2 utility clamps
- 10 mL graduated cylinder
- Methanol
- Deionized Water

Reagents and Properties

Substance	*Quantity*	*mol mass (g/mol)*	*bp (°C)*
Methanol	20 mL	32.04	64.7
Deionized Water	20 mL	18.02	100

Procedure

Assemble the distillation apparatus as seen in the example or also in Figure 3 in your book, using the 100 mL round bottom flask and a 10 mL graduated cylinder for the receiver. Place two boiling chips and 25 mL each of methanol and water into the flask. Start the flow of water though the condenser, making sure water is not leaking from the condenser. Heat the mixture to boiling, doing so slowly (set the regulator to 4). Record the temperature when the first drop distills, and again after every 0.5 mL of distillate is collected. Continue the distillation until ~5 mL remains in the pot.

Turn off the heater and let the flask cool down. Turn off the condenser, and reassemble the fractional distillation apparatus as seen in the example in lab or on Figure 4 in your book. Repeat the above procedure for the fractional distillation.

Remember to dispose of all liquids into their proper container. Plot your data in the format T vs. volume collected (see figure 6 in your lab manual) and turn the graphs in with your lab report. Using excel is highly encouraged. Comment on the differences between the fractional and simple distillations, and why they might be different.

Post Lab Questions

1. Plot the data for simple distillation and for fractional distillation on one graph. Plot temperature on the vertical axis and total volume of distillate on the horizontal axis, as shown in Figure 6 on page 28 in your lab manual. Draw a smooth curve through the data points for each distillation. Using Excel is recommended.
2. At what temperatures were the first drop of distillate collected in the simple and fractional distillations? Comment how they differ from the bp of methanol, and from each other. Is the difference between the simple and fractional initial boiling points what you would expect? Why or why not?
3. Compare the T vs. vol plot for your simple distillation with that for your fractional distillation. In which case is the more gradual temperature change observed? Which method is more effective in achieving separation? Briefly explain.

NUCLEOPHILIC SUBSTITUTION REACTIONS / ALKYL HALIDES

Nucleophilic substitution reactions are an important class of reactions which allow the displacement of one functional group or substituent on an sp^3-hybridized carbon atom with another.

$$\mathbf{Nu:^- + R_3C-X \longrightarrow R_3C-Nu + X^-}$$

The X group is called the leaving group. In this experiment, X is chloride, but can be any group which can accommodate a negative charge (X, an anion is formed). Nu:$^-$ is the nucleophile and is characterized by having an unshared pair of electrons which form a new bond with the carbon atom. Anions which can act as nucleophiles include halides, cyanide, hydroxide, alkoxide, and others. Neutral compounds which can act as nucleophiles include amines, alcohols, and water (with subsequent loss of a proton).

$$\mathbf{HNu: + R_3C-X \longrightarrow R_3C-NuH^+ + X^- \longrightarrow R_3C-Nu + HX}$$

Two classes of nucleophilic substitutions occur at sp^3-hybridized carbons: S_N1 and S_N2. In this experiment, you will investigate how reactivity and reaction rates are affected by the different structures of a group of alkyl chlorides under S_N1 and S_N2 conditions

S_N2 Reactions (substitution-nucleophilic-bimolecular)

S_N2 reactions occur as a concerted process. As the nucleophile approaches the carbon atom and bond forming begins, bond breaking between the carbon atom and the leaving group occurs simultaneously.

$$\mathbf{Nu:^- + C-X \longrightarrow [\,Nu\cdots C\cdots X\,] \longrightarrow Nu-C + X^-}$$

transition state *inverted configuration*

In the transition state both the nucleophile and leaving group are present, hence the kinetics are bimolecular and the reaction rate is proportional to both the concentration of the substrate and the concentration of the nucleophile. If you double the concentration of the nucleophile or the substrate, you double the reaction rate.

$$\mathbf{rate = k\,[Nu:^-]\,[Substrate]}$$

Factors other than reactant concentration that may affect S_N2 reaction rates include 1) leaving group ability 2) nucleophilicity of the nucleophile 3) stereochemistry and 4) nature of the solvent.

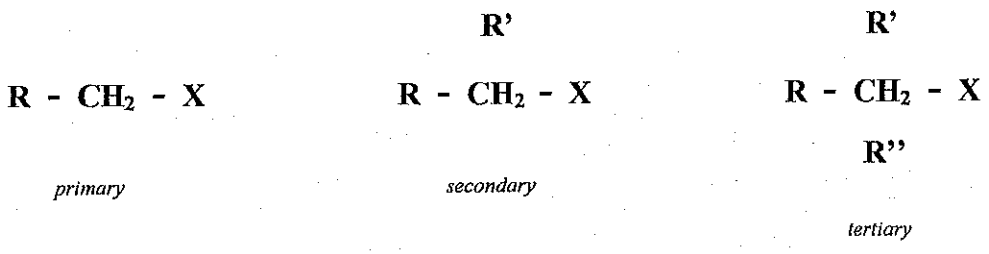
1) *leaving group ability* - The more an X is able to accommodate a negative charge, the better a leaving group it will be, and the faster the reaction. Anions of this type are weak bases (review acids and their conjugate bases). Leaving group ability in decreasing order is shown below for the halide series. Note that HI is the strongest acid of the group, so I^- is the weakest base and best leaving group.

$$\mathbf{I^- > Br^- > Cl^- > F^-}$$

2) *nucleophilicity of the nucleophile* - In general, the higher the basicity of a nucleophile, the more active it will be in displacing a leaving group. Therefore, HO^- is a better nucleophile than water because it is a stronger base. Basicity, thus nucleophilicity, tends to decrease from left to right across the periodic table. Nucleophilicity is shown below for a series of first row elements.

$$\mathbf{H_2N^- > HO^- > NH_3 > F^- > H_20}$$

3) *stereochemistry* - The incoming nucleophile can approach the reaction site only from the side opposite the leaving group. Any substituents which can block or hinder the approach of the nucleophile will slow the reaction (or prevent it from occurring altogether). Thus, S_N2 reactions occur only at primary and secondary carbon atoms (where the R groups do not impede the approach of the nucleophile), but never at tertiary carbons.



As a result of the backside attack by the nucleophile, inversion of configuration (Walden inversion) always occurs in S_N2 reactions.

4) *nature of the solvent* - The solvent in an S_N2 reaction must be polar enough to dissolve the nucleophile and stabilize anion formation, but not so polar as to promote ionization of the substrate. Usually, polar aprotic solvents, e.g. ethers or tertiary amides, are favored.

S_N1 Reactions (substitution-nucleophilic-unimolecular)

In contrast to S_N2 reactions, S_N1 reactions occur in two steps. In the first step (the rate determining step), the substrate ionizes to form a carbocation and an anion (from the leaving group). In the second step, the nucleophile attacks the carbocation, forming product.

$$R_3C-X \xrightarrow{\text{------}} R_3C^+ + X^- \xrightarrow{Nu:^-\ \text{------}} R_3C-Nu + X^-$$

Since only the substrate is involved in the rate determining step, the kinetics are unimolecular and the reaction rate is proportional only to substrate concentration.

$$\textbf{rate} = \textbf{k [substrate]}$$

Doubling the concentration of the substrate will double the rate of reaction, but changing the concentration of the nucleophile will have no effect on reaction rate. Note:do not confuse reaction rate with yield. A slow reaction can give a high yield if given a sufficient time to react. Yield is also affected by isolation techniques which have nothing to do with reaction kinetics.

The S_N1 mechanism is favored by any conditions which promote the formation of the carbocation. The structure of the substrate is of primary importance. Structures which ionize to form stable carbocations facilitate the S_N1 mechanism. Carbocations of decreasing stability as follows:.

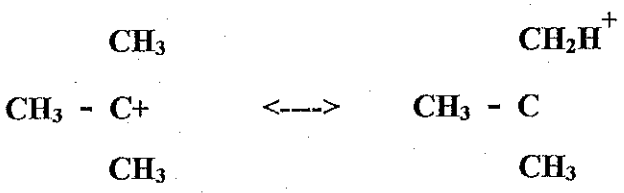
$$\underset{\textit{benzyl}}{-C^+H_2} > \underset{\substack{\textit{tertiary}\\ R''}}{\overset{R'}{R-C^+}} \sim \underset{\textit{allyl}}{CH_2=CH-C^+H_2} > \underset{\textit{secondary}}{\overset{R'}{R-C^+H}} > \underset{\textit{primary}}{RC^+H_2}$$

In general, when a charged species (a carbocation) is being formed, the delocalization of that charge over several atoms favors the formation of the charge. The benzylic and allylic carbocations shown above appear to be primary carbocations, but, in fact, are stabilized by resonance overlap with the pi electrons, which delocalizes the positive charge. Therefore, their formation is favored and benzylic and allylic compounds readily undergo S_N1 reactions, in addition to S_N2 reactions.

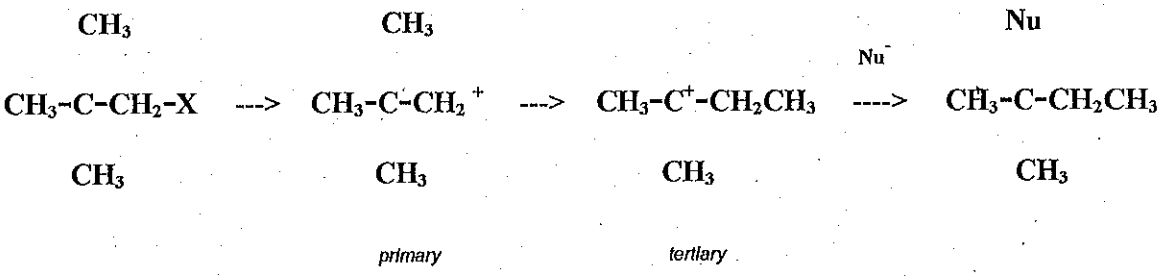
$$-C^+H_2 \longleftrightarrow =CH_2 \longleftrightarrow =CH_2 \longleftrightarrow =CH_2$$

$$CH_2=CH-C^+H_2 \longleftrightarrow {}^+CH_2-CH=CH_2$$

Reactions at tertiary carbons also occur under S_N1 conditions. First, steric hinderance prevents S_N2 attack. Second, tertiary carbocations are stabilized by hyperconjugation, overlap with the sigma electrons of the neighboring substituents which helps to delocalize the charge. Thus, nucleophilic substitution at a tertiary carbon occurs only by S_N1 chemistry.



Formation of secondary and primary carbocations is much less favored and S_N1 reactions occur only in those cases where steric hinderance inhibits S_N2 attack and an alkyl shift leads to a more stable tertiary carbocation.



Lastly, solvent can be important in facilitating an S_N1 reaction. Solvents which can help stabilize the carbocation are generally used and include polar, protic solvents, such as alcohols and water.

The stereochemistry of S_N1 reactions is also different from that of S_N2 reactions. The positively charged carbon atoms of carbocations are sp2 hybridized and are planar (all the substituents around the positively charged carbon atoms lie in the same plane). The incoming nucleophile can approach the carbon atom from either side of the plane giving a product mixture which is *50%* inverted and *50%* retained configuration. Such a mixture is called a racemate or racemic mixture. The product from an optically active starting material will lose its optical activity under S_N1 conditions, but show opposite optical activity under S_N2.

Experiments

Objective: to determine the effects of structure on the rate of reaction of various alkyl chlorides under S_N1 and S_N2 conditions.

Materials and Equipment:

1-chlorobutane	water bath *or*
2-chlorobutane	hot plates w/ 400 mL beaker
2-chloro-2-methylpropane	thermometer
3-chloropropene (allyl chloride)	small test tubes
18% sodium iodide in acetone	pasteur pipets and rubber bulbs
1% silver nitrate in ethanol	test tube rack

Students: Reagents are water sensitive. Please keep all containers closed as much as possible. All glassware very clean and dry.

Procedures:

S_N2 Reaction

Iodide ion is an excellent nucleophile and will displace chloride from alkyl chlorides. Acetone is used as a solvent because sodium iodide (NaI) is readily soluble and the product sodium chloride (NaCl) is not. Thus when NaI reacts with an alkyl chloride in acetone, a positive indication of reaction is the formation of an insoluble white solid. Anything from a slight haze to a heavy precipitate should be considered a positive result.

First, set up a *50°C* water bath. Fill a 400mL beaker with 200mL water and place it on a hot plate (setting of 2 to start). Monitor the temperature with a thermometer. If the temperature rises above *50°C,* turn down the heat and add some cold water to adjust the temperature. It is important not to overheat the bath because acetone readily evaporates and this may cause 'false positives'.

Label four test tubes, one for each alkyl chloride. Add 25 drops of 18% NaI in acetone to each test tube. Then add 6 drops of the appropriate alkyl chloride to each tube and mix by shaking back and forth, noting the time of addition. If a precipitate forms on the addition of the first few drops, but redissolves on shaking, ignore this. Time 2 minutes and note any changes. If nothing has happened, place the tubes in the water bath and again note the time to any changes. It is important to stay focused because changes may occur rapidly. Heat no longer than *5* minutes. Record the time to form a precipitate and under what conditions for each alkyl chloride.

Repeat the above experiment with 25 drops NaI in acetone and 18 drops of each alkyl chloride.

S_N1 Reaction

In the reaction of an alkyl chloride with silver nitrate ($AgNO_3$) to form silver chloride and an alkyl nitrate, the silver atom coordinates with the chloride facilitating the formation of the carbocation. Nitrate ion is such a weak nucleophile, that direct S_N2 displacement cannot occur.

$$R_3C\text{-}Cl + AgNO_3 \text{ -----> } R_3C^+ + AgCl + NO_3^-$$

1% $AgNO_3$ in ethanol is strictly S_N1 conditions. Again, a positive indication of reaction is the formation of a white precipitate (AgC1) ranging from a haze to a heavy solid. Ignore any precipitate which redissolves on mixing.

Label four test tubes, one for each alkyl chloride and add 25 drops 1% $AgNO_3$ in ethanol to each. Then add 6 drops of the appropriate alkyl chloride to each tube with shaking and note the time of addition. Time 2 minutes. If no change has occurred, place the tubes in the water bath and note the time to any changes. Heat no longer than 5 minutes.

Clean Up

Wash the test tubes into the waste solvent container. Glassware must be free of all chemical residue and contaminants before disposal in solid waste container.

Pre-lab Questions

1. Draw the structures of the alkyl chlorides in this lab and label the substitution (primary, secondary, tertiary, allyl).

2. Rank the order of reactivity you expect (fastest to slowest) for the alkyl chlorides when reacted with NaI in acetone.

3. Rank the order of reactivity you expect (fastest to slowest) for the alkyl chlorides when reacted with $AgNO_3$ in ethanol.

4. Predict the change, if any, in the following rates of reaction:

    a. The concentration of NaI reacted with 1-chlorobutane is doubled.

    b. The concentration of NaI reacted with 1-chlorobutane is doubled and the concentration of 1-chlorobutane is halved.

Post-lab Questions

1. Did your results confirm your expectations for the reactivity of the alkyl chlorides with NaI?

2. Did your results confirm your expectations for the reactivity of the alkyl chlorides with $AgNO_3$?

3. What changes in the rate of reaction occurred, if any, when the concentration of alkyl chloride was tripled in the reaction with NaI?

Bromination of *E*-Stilbene

For background information, see bromination, which exists in the book.

Updated Procedure

Materials and Equipment

100 mL Round Bottom Flask	Ice Bath
Condenser	250 mL Erlenmeyer flask
Rubber Tubing	Buchner Funnel w/ Filter Paper
Ethanol	Heating Mantle & Regulator
Bromine	Clamp
E-Stilbene	Ring Stand

Reagents and Properties

Substance	*Quantity*	*mol mass (g/mol)*	*bp (°C)*
Ethanol	10 mL	46.08	78.4
E-Stilbene	.500 g	180.25	122-125 (m.p.)
Bromine	3.0 mL	159.8	---

Procedure

Place 0.500 grams of *E*-Stilbene in a 100 mL Round-bottom flask. Add 10 mL of ethanol to the flask and clamp the flask to a ring stand. Add 2-3 boiling stones to the round bottom flask. Attach a reflux condenser to the flask and use a flask heater to heat the solution to reflux. Be sure that cold water is flowing through the condenser. Add 3.0 mL of the bromine/ethanol solution provided by Lab Services dropwise through the condenser. The reaction mixture may turn orange, but the color will fade to a cloudy white after further heating. Continue refluxing for one hour after the bromine solution has been added. Cool the reaction mixture, first to room temperature, then in an ice bath for 5-10 minutes. Collect the white crystals of dibromostilbene by vacuum filtration and wash with cold water. Allow the crystals to dry for 15-20 minutes. Record the yield and melting point. (Literature m.p. 241°C)

Post Lab Questions

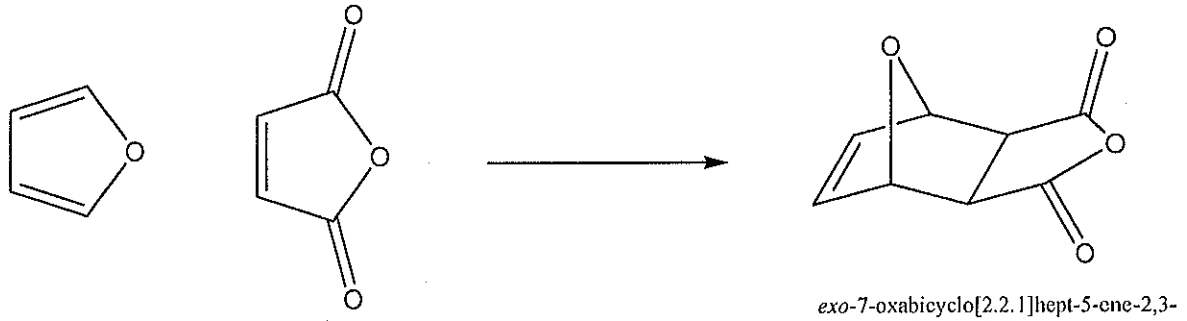
1. What is the % yield of your reaction?

2. Propose a reasonable mechanism for this reaction.

3. The product contains two setereocenters. Is the product optically active? Explain your answer.

Diels-Alder

For background information, see pgs. 101-103 of your lab book.



furan maleic anhydride

exo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride

Materials and Equipment

Furan	Scintillation Vial
Tetrahydrofuran	125 mL Erlenmeyer flask w/ side arm
Maleic Anhydride	Buchner Funnel
Melting Point Apparatus	

Reagents and Properties

Substance	*Quantity*	*mol mass (g/mol)*
Furan	1.7 mL	68.03
Tetrahydrofuran	15 mL	70.05
Maleic Anhydride	2.5 g	98.00

Procedure

Week 1: Weigh out 2.5 g of maleic anhydride and add it to the scintillation vial. Add into the vial 8 mL of tetrahydrofuran (THF) and 1.5 mL of furan. Thoroughly mix the products. Cap the vial and make sure to label it with your lab group. Place the vial in the designated spot where your TA tells you.

Week 2: Assemble a filtering apparatus. Wet the filter paper with 5 mL of cold THF. Filter your product, making sure to get all of the crystals out. Let stand for 5 minutes to thoroughly dry. Mass your crystals to obtain a % yield. Take a melting point of both your compound and maleic anhydride. Your product is called *exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride. Its literature melting point is 116-117 °C.

Post Lab Questions

1. Calculate the percent yield for your product. Discuss why it might not be 100%.
2. Compare the melting point of your product to that of literature.
3. The product of this reaction can be hydrolyzed by water. Show the product of hydrolysis.
4. Recrystallizing an anhydride (such as the product of this reaction) from water or from an alcohol is rarely a good idea. Explain why (drawing a reaction might be a good idea).

Stereoisomerism:

NAME _____ SECTION _____

1 ***A Chiral Center***

1. _____ 2. _____
3. _____
4. _____
5. _____

1-bromobutane

2-bromobutane

1,2-dibromobutane

1,3-dibromobutane

1,4-dibromobutane

2,3-dibromobutane

2 ***Chirality and Enantiomers***

6. _____
7. _____
8. _____
9. _____
10. _____
11. _____ 12. _____
13. _____ 14. _____

3

Diastereomers and Meso Forms

15. _____

16. _____

17. _____ 18. _____

19. _____ 20. _____

21. _____ 22. _____

23. _____ 24. _____

25. _____ 26. _____

27. _____

28. _____ 29. _____

30.

31. _____

4

The R–S Convention

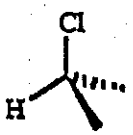
32. _____

33. _____

34. _____ 35. _____

36. >

37.



38. _____ 39. _____

40. _____