Please print the first three letters of your last name in the three boxes

Please Note: This test may be a bit long, but there is a reason. I would like to give you a lot of little questions, so you can find ones you can answer and show me what you know, rather than just a few questions that may be testing the one thing you forgot. I recommend you look the exam over and answer the questions you are sure of first, then go back and try to figure out the rest. Also make sure to look at the point totals on the questions as a guide to help budget your time.

You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK will be regraded.

Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.

FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENCTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!
<table>
<thead>
<tr>
<th>Page</th>
<th>Points</th>
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</thead>
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<td>(18)</td>
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<td>4</td>
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<td>(12)</td>
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<tr>
<td>Total</td>
<td>(387)</td>
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</tbody>
</table>
Honor Code

The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.

____________________________
(Your signature)
The first semester of Organic Chemistry is a journey that begins with a review of material you have seen, transitions to the study of organic molecules, then settles in with a long discussion of reactions and their mechanisms. The pace accelerates through the chapters until we get to the chemistry of epoxides. We finish with a chapter on NMR, the point of which is determining molecular structure. Solving organic synthesis problems requires not only a firm command of the many reactions and mechanisms we have presented, but also high level problem solving skills and a spark of creativity. You have all come a long way since late August when you first came to class. It is my sincere hope that this final serves to affirm that you have completed this journey successfully and caught the Organic Chemistry wave!

As you go through the test, use good test taking strategy by:
  1) Remaining as relaxed and calm as possible
  2) Working problems worth the most points first
  3) Concentrate on finishing all the problems you are most certain about
  4) Leave the ones you have doubts about for last
  5) Do not second guess yourself

Have a safe holiday and remember to exercise every chance you get.

*If you stay in shape throughout your life, you will thank yourself more than you can imagine!!!*

Brent Iverson
Use this page to write down your roadmap if you would like.
Use this page for scratch if you would like. For your reference, here are the Golden Rules of Chemistry:

1. Atoms prefer filled valence shells.  
2. The most important question in chemistry is "Where are the electrons?"  
5. Most reactions involve nucleophiles (molecules with a location of particularly high electron density) attacking electrophiles (molecules with a location of particularly low electron density).  
6. Steric interactions (atoms bumping into each other) can prevent reactions by keeping the reactive atoms away from each other.  
7. Pi electrons prefer to be delocalized over as many adjacent sp$^2$ hybridized atoms (or sp$^1$ hybridized atoms in some cases) as possible, and aromaticity is the most stable form of pi electron delocalization.
### PERIODIC TABLE OF THE ELEMENTS

#### Elementary Subatomic Particles

<table>
<thead>
<tr>
<th>Column</th>
<th>Subatomic Particle</th>
<th>Charge</th>
<th>Mass Number</th>
<th>Proton Number</th>
<th>Neutron Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Proton</td>
<td>+1</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Neutron</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>Electron</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

#### % Ionic Character of a Single Chemical Bond

<table>
<thead>
<tr>
<th>Column</th>
<th>Ionic Character</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0%</td>
<td>Weak bonds</td>
</tr>
<tr>
<td>2</td>
<td>10%</td>
<td>Medium bonds</td>
</tr>
<tr>
<td>3</td>
<td>20%</td>
<td>Strong bonds</td>
</tr>
<tr>
<td>4</td>
<td>30%</td>
<td>Very strong bonds</td>
</tr>
</tbody>
</table>

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**Editor:** T. K. Varga, M.A.Sc. & C. Bell, M.A.Sc.  
**Copyright:** 2001 Papertech  
**ISBN:** 0-88006-275-6  
<table>
<thead>
<tr>
<th>Type of Hydrogen (R = alkyl, Ar = aryl)</th>
<th>Chemical Shift (δ)*</th>
<th>Type of Hydrogen (R = alkyl, Ar = aryl)</th>
<th>Chemical Shift (δ)*</th>
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<tbody>
<tr>
<td>R₂ NH</td>
<td>0.5-5.0</td>
<td>RCH₂ OH</td>
<td>3.4-4.0</td>
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<tr>
<td>ROH</td>
<td>0.5-6.0</td>
<td>RCH₂ Br</td>
<td>3.4-3.6</td>
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<td>RCH₂ Cl</td>
<td>3.6-3.8</td>
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<td>1.2-1.4</td>
<td>RCOCH₃</td>
<td>3.7-3.9</td>
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<tr>
<td>R₃ CH</td>
<td>1.4-1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R₂ C=CRCHR₂</td>
<td>1.6-2.6</td>
<td>RCOCH₂ R</td>
<td>4.1-4.7</td>
</tr>
<tr>
<td>RC≡CH</td>
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<td>RCH₂ F</td>
<td>4.4-4.5</td>
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<tr>
<td>RCCH₃</td>
<td>2.1-2.3</td>
<td>ArOH</td>
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<tr>
<td>RCCH₂ R</td>
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<td>R₂ C=CH₂</td>
<td>4.6-5.0</td>
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<tr>
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<td>R₂ C=CHR</td>
<td>5.0-5.7</td>
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<tr>
<td>RCH₂ NR₂</td>
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<td></td>
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<tr>
<td>RCH₂ I</td>
<td>3.1-3.3</td>
<td></td>
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<tr>
<td>RCH₂ OR</td>
<td>3.3-4.0</td>
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* Values are relative to tetramethylsilane. Other atoms within the molecule may cause the signal to appear outside these ranges.
<table>
<thead>
<tr>
<th>Compound</th>
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<tr>
<td>Protonated alcohol</td>
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<tr>
<td>Hydronium ion</td>
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<tr>
<td>Acetic acid</td>
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<tr>
<td>Ammonium ion</td>
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<td>Thiols</td>
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<tr>
<td>β-Dicarboxyls</td>
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<tr>
<td>Ethyl ammonium ion</td>
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<tr>
<td>β-Ketoesters</td>
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<tr>
<td>β-Diesters</td>
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<tr>
<td>Water</td>
<td>15.7</td>
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<td>Alcohols</td>
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<tr>
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<td>Terminal alkynes</td>
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<tr>
<td>LDA</td>
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<tr>
<td>Terminal alkenes</td>
<td>44</td>
</tr>
<tr>
<td>Alkanes</td>
<td>51</td>
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1. (5 pts) What is the most important question in organic chemistry?

2. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges. For the two structures on the left in each problem, use arrows to indicate the movement of electrons to give the structures you drew. There is no need to draw any circles around any of these contributing structures. You might want to read these directions again to make sure you know what we want.

3. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here and your answer should match a recent Rule of the Day.
4. (2 pts each) In the spaces provided, indicate the type of bond, and the hybridized orbitals that overlap to form the bond. For example, one answer could be: $\sigma_{\text{Csp}^3-H1s}$

Clavulanic Acid
(A drug developed to overcome certain types of antibiotic resistance)

5. (2 pts each) In the spaces provided, write the hybridization state of the atoms indicated by the arrow.
6. (1 pt each) **Circle all the True statements.** (Do not circle any false statements) You may notice these resemble Rules of the Day! These are worth a lot of points so please take your time and be careful. Read them carefully, but do not second guess yourself as we are not trying to trick you.

A. More electronegative atoms attract the majority of electron density in a bond, thereby answering the most important question in chemistry.

B. A sigma bond has the majority of electron density above and below the bond axis, while a pi bond has the majority of electron density between atomic nuclei.

C. Constitutional isomers are molecules with the same molecular formula, but have the atoms connected differently.

D. The preferred staggered conformations of butane are the "gauche" conformations, rather than the "anti" conformation.

E. Stereoisomers have the same connectivity (they are the same constitutional isomer), but the atoms are arranged differently in space.

F. Dispersion forces are proportional to surface area, so the smaller the surface area of an alkane, the greater the attraction between molecules and the higher the boiling point.

G. Substituted cyclohexanes prefer to have as many substituents axial as possible, with the larger substituents dominating.

H. *Trans* alkenes are more stable than *cis* alkenes because *cis* alkenes have some non-bonded interaction strain.

I. The enol form of a compound rapidly tautomerizes to the more stable keto form.

J. The keto form of a compound rapidly tautomerizes to the more stable enol form.

K. The keto form of a compound rapidly mesmerizes to the more stable enol form.

L. In organic synthesis, A KEY PARADIGM is the that functional groups (OH group, Pi bond of an alkene, etc.) react the same in large complex molecules as they do in simple structures.

M. Ethers can be synthesized using an $S_N2$ reaction between a primary alkyl halide and an alkoxide (called the Williamson ether synthesis)

N. Ethers are synthesized using an $S_N1$ reaction between a tertiary alkyl halide and an alkoxide (called the Williamson County ether synthesis)

O. Epoxides are important because the ring strain within epoxides allows them to react with nucleophiles.

P. A $^1$H nucleus surrounded by greater electron density is considered to be more shielded and comes into resonance (absorbs electromagnetic radiation) at a lower frequency (smaller ppm).

Q. "Resonance" in NMR refers to the phenomenon of absorption of energy when a nuclear spin "flips".

R. Running 3-5 miles a week EVERY WEEK as an adult dramatically increases your fitness level and improves your health throughout your life. Doing this and enjoying a healthy life is even more important than getting an A on this organic final!
8. (15 pts total) On the following three pages there are NMR spectra. The relative integrations are given above each signal. Assign each spectra to the appropriate structure out of the following possibilities. Each NMR spectrum has a letter on it. Write the appropriate letter underneath the molecules in the space provided. Notice that not all of the molecules below will have letters underneath them, as there are only three spectra but seven molecules. Note that you are allowed to write each letter only once or it will be marked wrong.
B

[Chemical spectrum diagram with peaks labeled 2H, 3H, and 2H 2H 3H, PPM scale from 0 to 3]
9. The following molecule is called glutathione. It is found in high concentration in living cells where it helps maintain the proper oxidation potential as well as providing protection from oxidants such as free radicals. **In the boxes, fill in the proper number of bonds to H atoms, lone pairs, and formal charges to show the protonation state of glutathione at pH 7.0.** Use the pK\textsubscript{a} table provided at the beginning of the test for reference.

A. (8 pts)

![Glutathione structure](image)

B. (1 pt) **What is the total charge on glutathione at pH 7.0?**

C. (1 pt) **How many chiral centers does glutathione have?**

D. (2 pt) **Glutathione is found as the single stereoisomer shown. Write an "R" or "S" next to each chiral center on the structure above.**

10. (16 pts total) The following are contributing structures for important resonance hybrids. Draw the other important resonance contributing structure in the box provided. Draw arrows on the structures on the left that indicate the flow of electrons that produce the contributing structures you drew to the right. Be sure to show all lone pairs and formal charges.

A.

![Resonance structure A](image)

*Did you remember to put arrows on the structures on the left?*

---

B.

![Resonance structure B](image)

*Yes, put arrow(s) on this structure to show how it is transformed to the structure to the far right!*

---

C.

![Resonance structure C](image)
11. (5 pts) A hydrogen bond is the strongest interaction seen among neutral molecules. In the space provided, draw two molecules of methanol (CH₃OH) and show a hydrogen bond between them. Use a dashed line (-----) to indicate the hydrogen bond. Show all lone pairs.

12. (12 pts. total) Rank the following species in terms of the stated property from 1 to 4 with intermediate numbers to rank the species of intermediate stability activity. Please make sure you know what we want, as you will get no credit if you get the numbers backwards!

**Radical Stability:** Place a 1 under the most stable radical and a 4 under the least stable radical.

```
   H     H₃C     H₃C     H₃C
  /\   /\   \   /\   \   /\   \   /\   /
 H₃C /\ C--CH H₃C /\ C--CH H₃C /\ C--CH₃
```

**Reaction with nucleophiles:** Place a 1 under the molecule that is most reactive in an S_N2 reaction and a 4 under the molecule that is least reactive in an S_N2 reaction.

```
     Cl     Cl     Cl     I
```

**Reaction in an S_N1/E1 reaction:** Place a 1 under the molecule that is most reactive in an S_N1/E1 reaction and a 4 under the molecule that is least reactive in an S_N1/E1 reaction.

```
     Cl     Cl     Cl     I
```
13. (5, 6 or 8 pts each) The following reactions all involve chemistry of alkyl halides. **Fill in the box above the arrow with the mechanism that will be followed** (S_N2, E2, etc.). **Then draw only the predominant product or products** and please remember that **you must draw the correct stereoisomers**. For S_N1/E1 reactions you must draw all significant products (including all stereoisomers).

A. 

\[ \text{Br} + \text{CN} \rightarrow \]

B. 

\[ \text{Br} + \text{CN} \rightarrow \]

C. 

\[ \text{Br} + \text{OH} \rightarrow \text{(assume no rearrangement)} \]

Repeat the last one, but only draw rearranged products

D. 

\[ \text{Br} + \text{OH} \rightarrow \text{(assume rearrangement)} \]

(2 pts) **For the reagents listed in parts C and D, how many total different products will be made if the reaction proceeds both with and without rearrangement?**
14. (8 pts total) On the line provided, state the stereochemical relationship between each pair of molecules: enantiomers, diastereomers, or the same molecule. I recommend you assign R and S to each chiral center to help answer this question. Circle all meso compounds.

(8 pts) In the two spaces below, draw the two equilibrating chair structures for the following cyclohexane derivative. Circle the one that predominates at equilibrium.
15. (26 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) For the following reactions, fill in the details of the mechanism. Draw the appropriate chemical structures and use an arrow to show how pairs of electrons are moved to make and break bonds during the reaction. For this question, you must draw all molecules produced in each step (yes, these equations need to be balanced!). Finally, fill in the boxes adjacent to the arrows with the type of step involved, such as "Make a bond" or "Take a proton away". Use wedges and dashes to indicate stereochemistry where appropriate, BUT if an intermediate or product is really a racemic mixture, you only need to draw one enantiomer and write racemic for this problem (we are making this easier for you).

For this next one you do not need to describe the reaction using one of the four fundamental mechanistic steps ("Make a bond", etc.)
15. (27 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) For the following reactions, fill in the details of the mechanism. Draw the appropriate chemical structures and use an arrow to show how pairs of electrons are moved to make and break bonds during the reaction. For this question, you must draw all molecules produced in each step (yes, these equations need to be balanced!). Finally, fill in the boxes adjacent to the arrows with the type of step involved, such as "Make a bond" or "Take a proton away". Use wedges and dashes to indicate stereochemistry where appropriate, BUT if an intermediate or product is really a racemic mixture, you only need to draw one enantiomer then label it racemic for this problem (we are making this easier for you).

**Acid-catalyzed ether formation**

```

```

**Epoxide opening in base**

```

```

Products
16. (3, 4 or 5 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.
17. (3 or 5 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.
18. (3, 4 or 5 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.

\[ \text{Signature} \]
19. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate.

A) (10 pts)

\[
\begin{array}{c}
\text{?} \\
\text{?} \\
\text{?}
\end{array}
\]

B) (10 pts)

\[
\begin{array}{c}
\text{?} \\
\text{?} \\
\text{?}
\end{array}
\]

Racemic
19. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

C) (15 pts)
19. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

D) (12 pts)
19. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

E) (7 pts)

\[ \text{Racemic} \]

F) (4 pts)
20. A number of molecules are dangerous because they make a covalent bond to DNA, causing a mutation when the cell with the modified DNA divides. A characteristic of these molecules is that they are electrophiles. Often, they interact strongly with the DNA before the covalent bond forms. This so-called preassociation greatly speeds up the reaction and helps target the DNA. A potent carcinogen is the benzopyrene diol epoxide. It is a metabolized byproduct of benzopyrene, a compound found in barbecued meats cooked over an open hot flame.

The large flat overall structure of the molecule helps it slip between the stacked base pairs of the DNA double helix, then the DNA reacts as a nucleophile with the benzopyrene diol epoxide.

Which of these products could be produced when the benzopyrene diol epoxide stereoisomer shown above reacts with DNA?

A) Only product C could be produced
B) Only A and B could be produced
C) Only C and D could be produced
D) All four are produced.
It turns out that many other electrophiles are dangerous as well. The nerve gas Sarin as well as the chemical warfare agent mustard gas are both electrophiles. In each case, these electrophiles react with important molecules in our bodies. The new covalent bonds that form inactivate the important molecules, explaining why Sarin and mustard gas are so deadly. For protection, our bodies have catalysts called glutathione S-transferases that react with electrophiles and prevent their doing damage. It is critical that you can quickly identify nucleophiles and electrophiles in reactions. Find the answer that best describes the following reaction:

\[
\text{S}^- + \text{Cl}^- \rightarrow \text{S}^- + \text{Cl}^-
\]

A) In this reaction, the negatively charged S atom is the nucleophile and so is the chloroalkane
B) In this reaction, the negatively charged S atom is the nucleophile, and the chloroalkane is the electrophile
C) In this reaction, the negatively charged S atom is the electrophile, and the chloroalkane is the nucleophile
D) In this reaction, the negatively charged S atom is the electrophile and so is the chloroalkane

It is essential that you learn to recognize nucleophiles and electrophiles. Below are two potential nucleophiles:

A) The structure labeled A is a better nucleophile compared to B.
B) The structure labeled B is a better nucleophile compared to A.
C) The structure labeled A and the structure labeled B are equally strong nucleophiles.
D) Neither structure is a nucleophile.

Consider the following series of molecules we have seen this semester:

A) Structures C, D, and E are electrophiles, while structures A, B and F are nucleophiles.
B) Structures A, B, C and E are electrophiles, while structures D and F are nucleophiles.
C) Structures B, C and E are electrophiles, while structures A, D and F are nucleophiles
D) Structures B and E are electrophiles, while structures A, C, D and F are nucleophiles