

NAME (Print): \_\_\_\_\_

Chemistry 320N  
Dr. Brent Iverson  
3rd Midterm  
April 18, 2013

SIGNATURE: \_\_\_\_\_

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

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|  |  |  |
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**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 INCIDENTS 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!!!**

| Page         | Points       |
|--------------|--------------|
| <b>1</b>     | <b>(26)</b>  |
| <b>2</b>     | <b>(13)</b>  |
| <b>3</b>     | <b>(10)</b>  |
| <b>4</b>     | <b>(24)</b>  |
| <b>5</b>     | <b>(14)</b>  |
| <b>6</b>     | <b>(26)</b>  |
| <b>7</b>     | <b>(20)</b>  |
| <b>8</b>     | <b>(15)</b>  |
| <b>9</b>     | <b>(16)</b>  |
| <b>10</b>    | <b>(17)</b>  |
| <b>11</b>    | <b>(10)</b>  |
| <b>12</b>    | <b>(13)</b>  |
| <b>13</b>    | <b>(19)</b>  |
| <b>14</b>    | <b>(9)</b>   |
| <b>Total</b> | <b>(232)</b> |

## **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.

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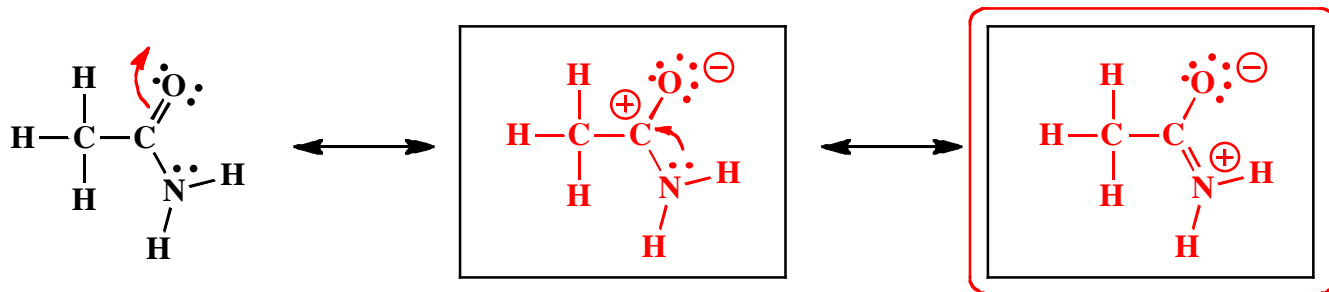
(Your signature)

| Compound           |   | pK <sub>a</sub> |
|--------------------|---|-----------------|
| Hydrochloric acid  | $\text{H-Cl}$   | -7              |
| Protonated alcohol | $\text{RCH}_2\text{OH}_2^+$   | -2              |
| Hydronium ion      | $\text{H}_3\text{O}^+$  | -1.7            |
| Carboxylic acids   | $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$   | 3-5             |
| Ammonium ion       | $\text{H}_4\text{N}^+$  | 9.2             |
| β-Dicarbonyls      | $\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$   | 10              |
| Primary ammonium   | $\text{H}_3\text{N}^+\text{CH}_2\text{CH}_3$  | 10.5            |
| β-Ketoesters       | $\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$  | 11              |
| β-Diesters         | $\text{ROC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$ | 13              |
| Water              | $\text{HOH}$  | 15.7            |
| Alcohols           | $\text{RCH}_2\text{OH}$   | 15-19           |
| Acid chlorides     | $\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$  | 16              |
| Aldehydes          | $\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$   | 18-20           |
| Ketones            | $\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$  | 18-20           |
| Esters             | $\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$  | 23-25           |
| Terminal alkynes   | $\text{RC}\equiv\text{C}-\text{H}$  | 25              |
| LDA                | $\text{H}-\text{N}(\text{i-C}_3\text{H}_7)_2$   | 40              |
| Terminal alkenes   | $\text{R}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{H}$   | 44              |
| Alkanes            | $\text{CH}_3\text{CH}_2-\text{H}$   | 51              |

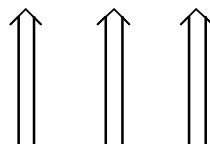
1. (2 pts) What is the most important question in chemistry?

**Where are the electrons?**

2. (8 pts) On the left is drawn the Lewis structure of a simple amide. Draw the two next most important contributing structures in the spaces provided. Be sure to show all lone pairs and formal charges. You do not need to draw arrows on the structures, but you can if it helps you.

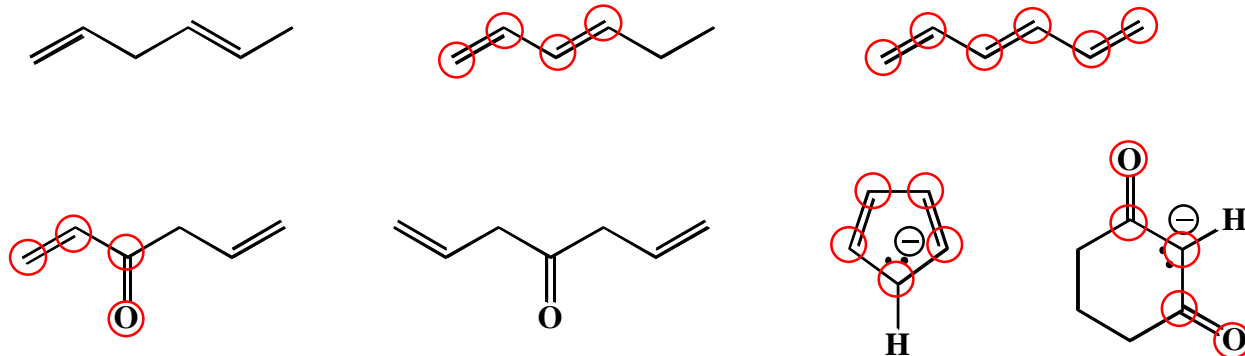


3. (2 pts) An important feature of an amide bond is that there is a partial double bond between the carbonyl carbon and nitrogen. For the contributing structures you drew in Problem 2., draw a circle around the one that predicts this partial double bond.



**Notice This**

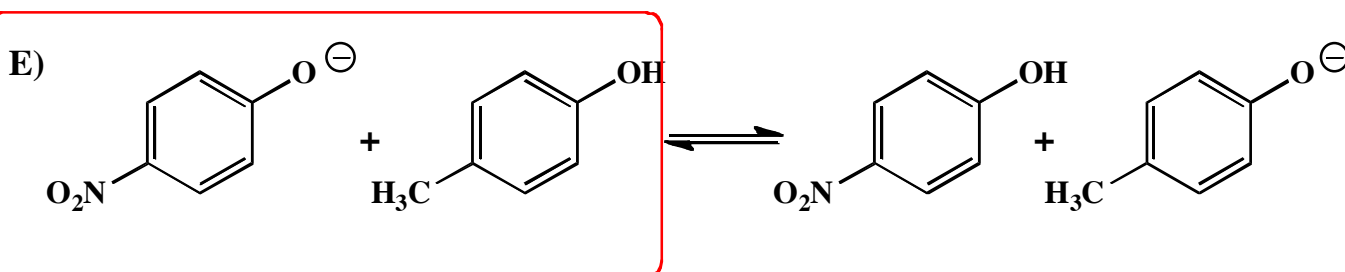
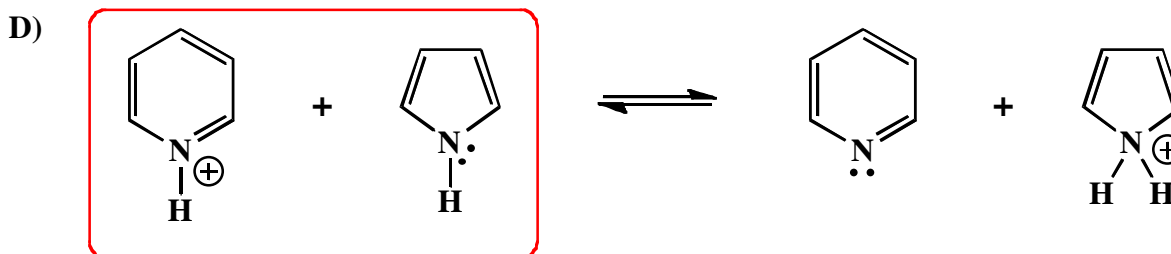
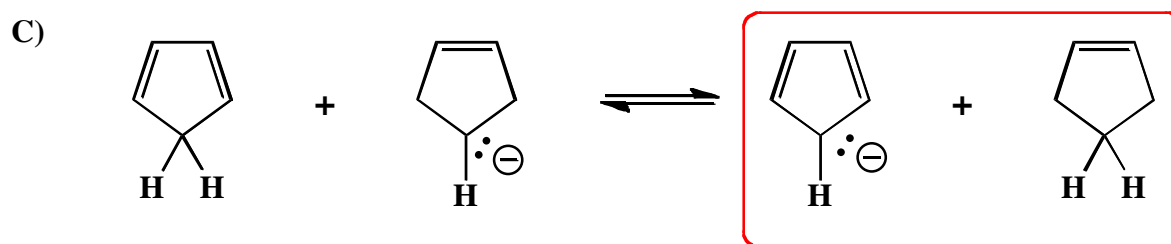
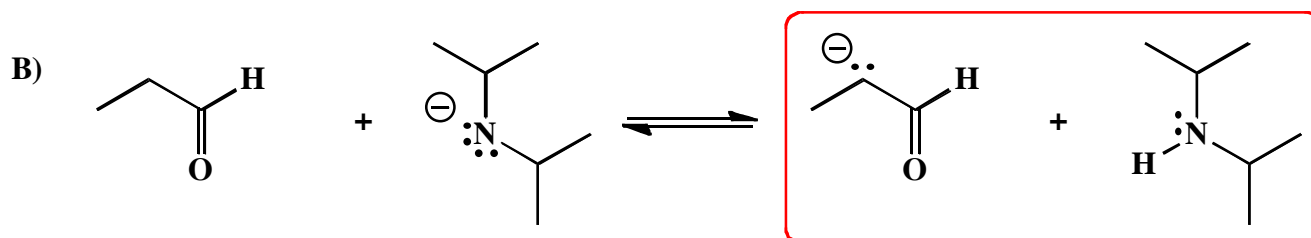
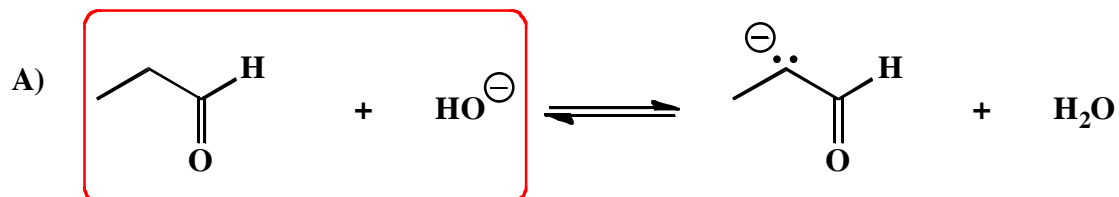
4. (14 pts) On the following structures, circle all the **atoms** that have atomic orbitals that are involved in the **DELOCALIZED** pi electron orbitals ( $\pi$ -ways). In other words, there has to be pi electron delocalization over three or more atoms in a molecule for any atoms to be circled.



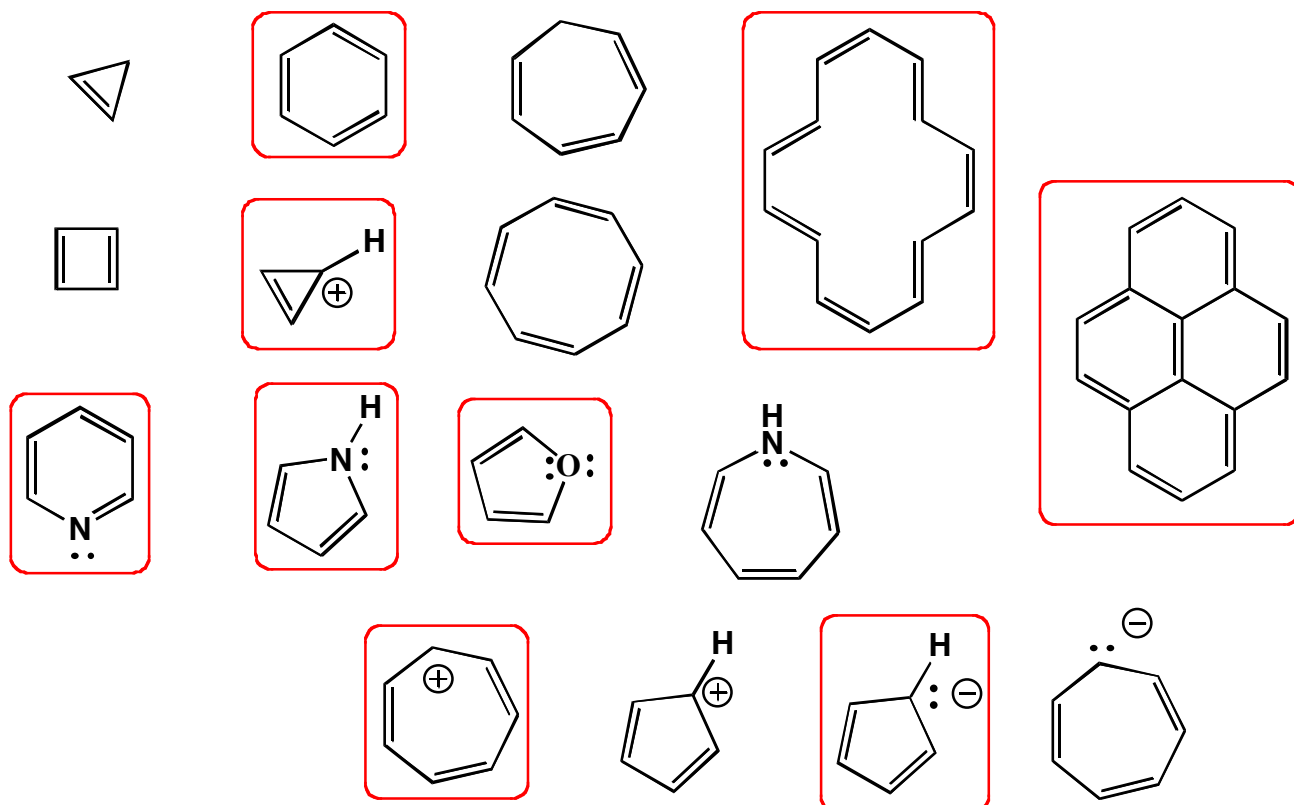
**5. (1 pt. each)** Here are a number of statements regarding aromaticity or other general aspects of organic chemistry. Do not second guess yourself, this is not meant to be tricky! **Check the appropriate box to indicate whether the statement is true or false.**

|  | True                                | False                               |
|--|-------------------------------------|-------------------------------------|
| A. When molecules absorb light, electrons are excited from a bonding to an antibonding molecular orbital.  | <input checked="" type="checkbox"/> | <input type="checkbox"/>            |
| B. The first step of the electrophilic aromatic substitution reaction involves a wicked strong electrophile reacting with pi electron density to create an arenium ion intermediate. | <input checked="" type="checkbox"/> | <input type="checkbox"/>            |
| C. The arenium ion intermediate has partial positive charge localized ortho and para to the location of the bound electrophile, but not meta.  | <input checked="" type="checkbox"/> | <input type="checkbox"/>            |
| D. The arenium ion intermediate has partial positive charge localized meta to the location of the bound electrophile, but not ortho and para.  | <input type="checkbox"/>            | <input checked="" type="checkbox"/> |
| E. Benzyl cations and radicals are stabilized by delocalization into the aromatic pi system.   | <input checked="" type="checkbox"/> | <input type="checkbox"/>            |
| F. The phenoxide anion is stabilized by delocalization into the aromatic pi system.  | <input checked="" type="checkbox"/> | <input type="checkbox"/>            |
| G. "Good" groups direct incoming wicked strong electrophiles ortho and para primarily because of an interaction referred to as pi donation.  | <input checked="" type="checkbox"/> | <input type="checkbox"/>            |
| H. "Good" groups are activating because they stabilize arenium ion intermediates   | <input checked="" type="checkbox"/> | <input type="checkbox"/>            |
| I. "Bad" groups direct wicked strong electrophiles meta primarily because of an interaction referred to as pi donation.  | <input type="checkbox"/>            | <input checked="" type="checkbox"/> |
| J. "Ugly" groups direct incoming wicked strong electrophiles ortho and para primarily because of the inductive effect.   | <input type="checkbox"/>            | <input checked="" type="checkbox"/> |
| K. "Ugly" groups are activating because they stabilize arenium ion intermediates.  | <input type="checkbox"/>            | <input checked="" type="checkbox"/> |
| L. "Ugly" groups are deactivating primarily because of the inductive effect.   | <input checked="" type="checkbox"/> | <input type="checkbox"/>            |
| M. The weather was perfect and the Longhorn run was a blast!   | <input checked="" type="checkbox"/> | <input type="checkbox"/>            |

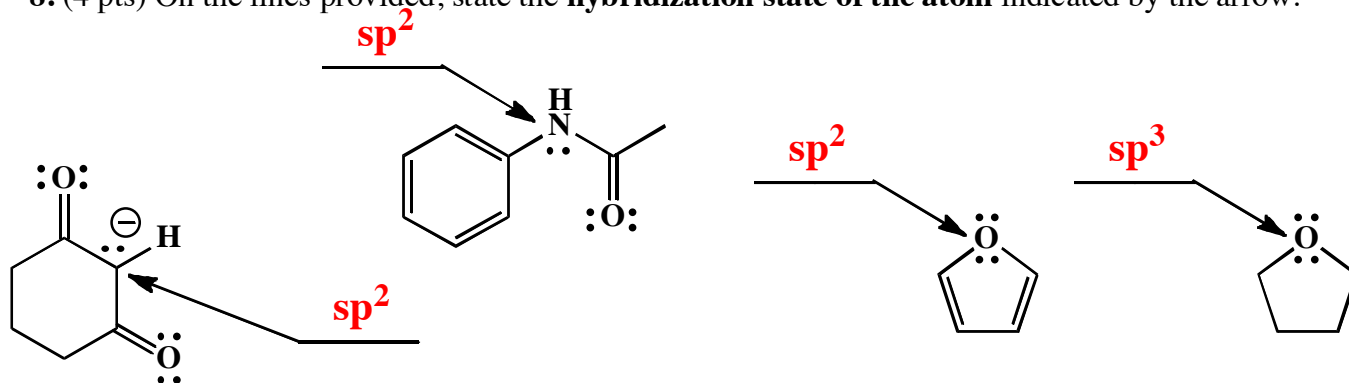
6. (2 pts each) For the following acid-base reactions, circle the side of the equation that is favored at equilibrium.



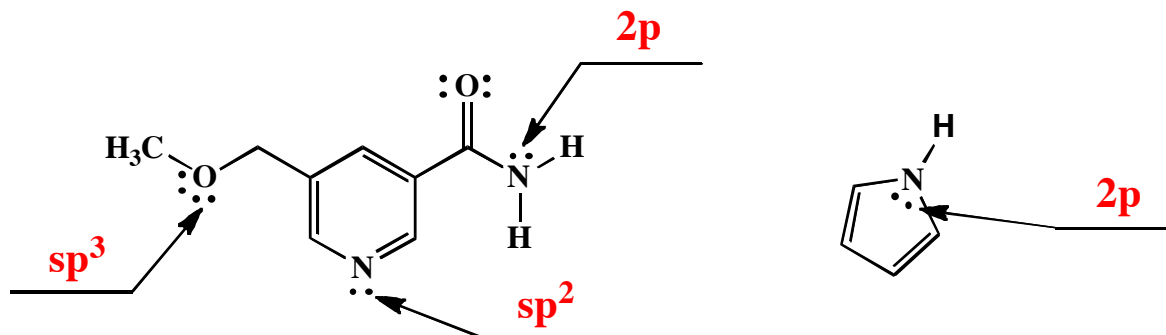
7. (16 points) Draw a circle around all of the molecules below that can be considered aromatic.



8. (4 pts) On the lines provided, state the hybridization state of the atom indicated by the arrow.

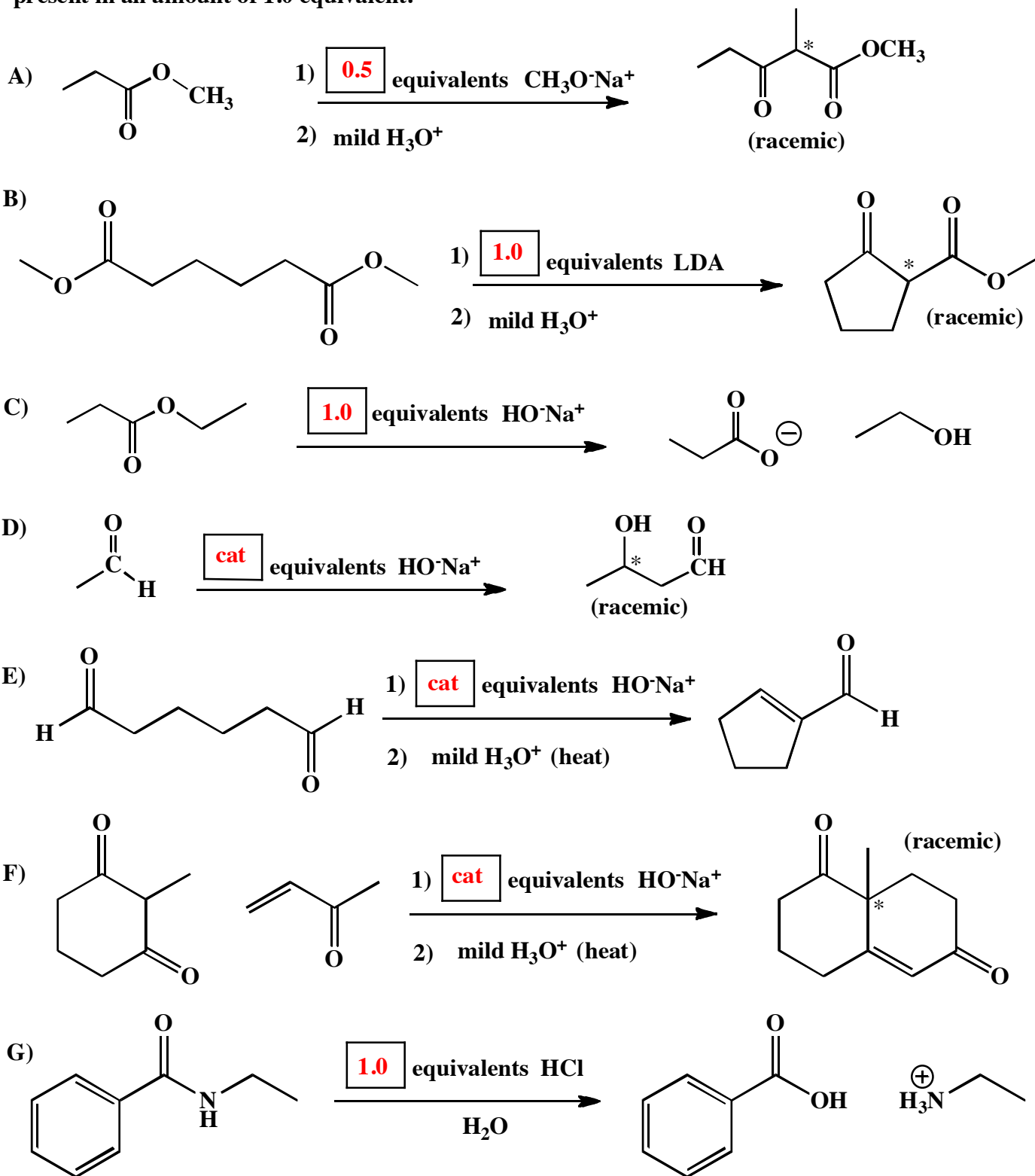


9. (4 pts) On the lines provided, state the atomic orbital that contains the lone pair of electrons indicated by the arrow.

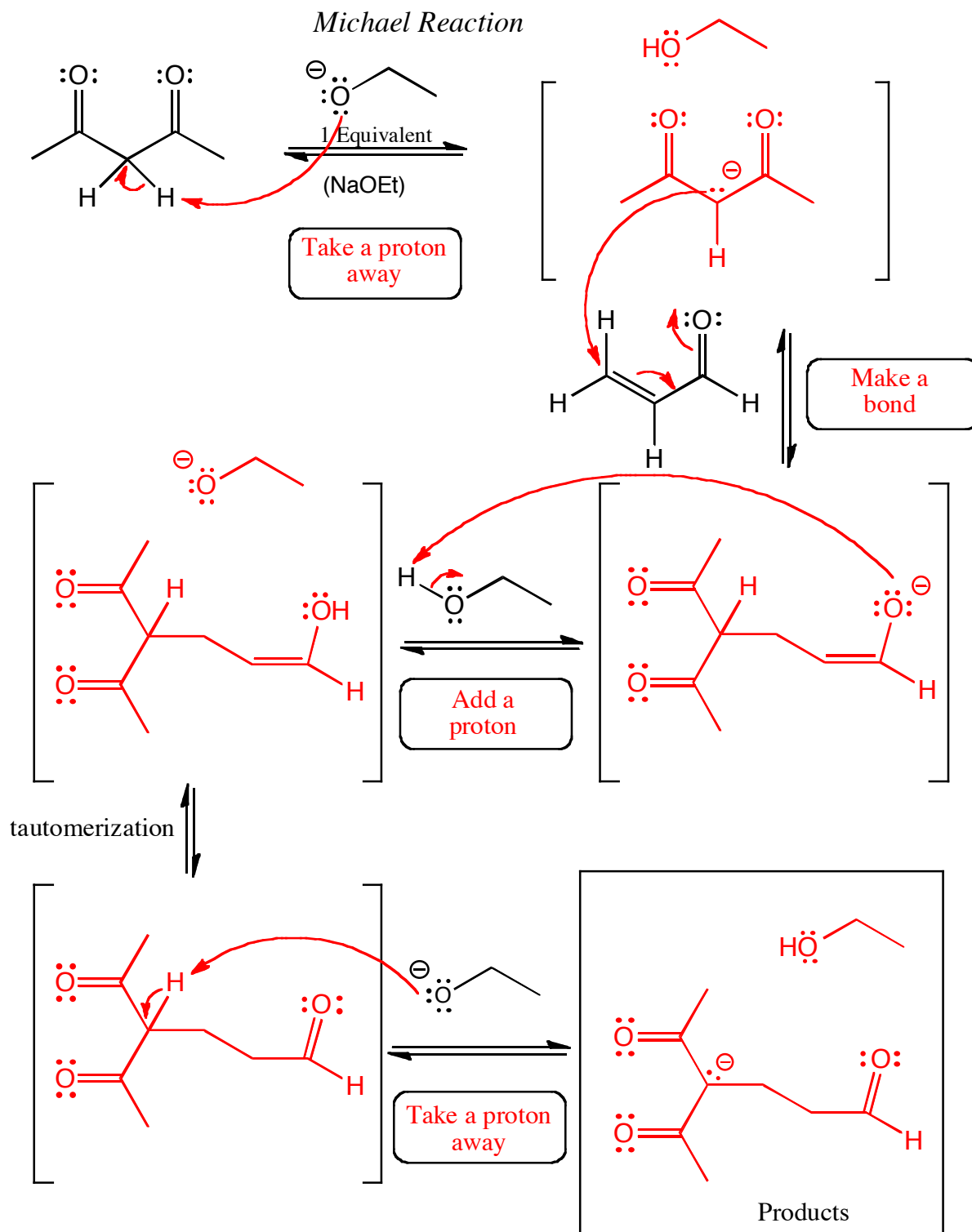




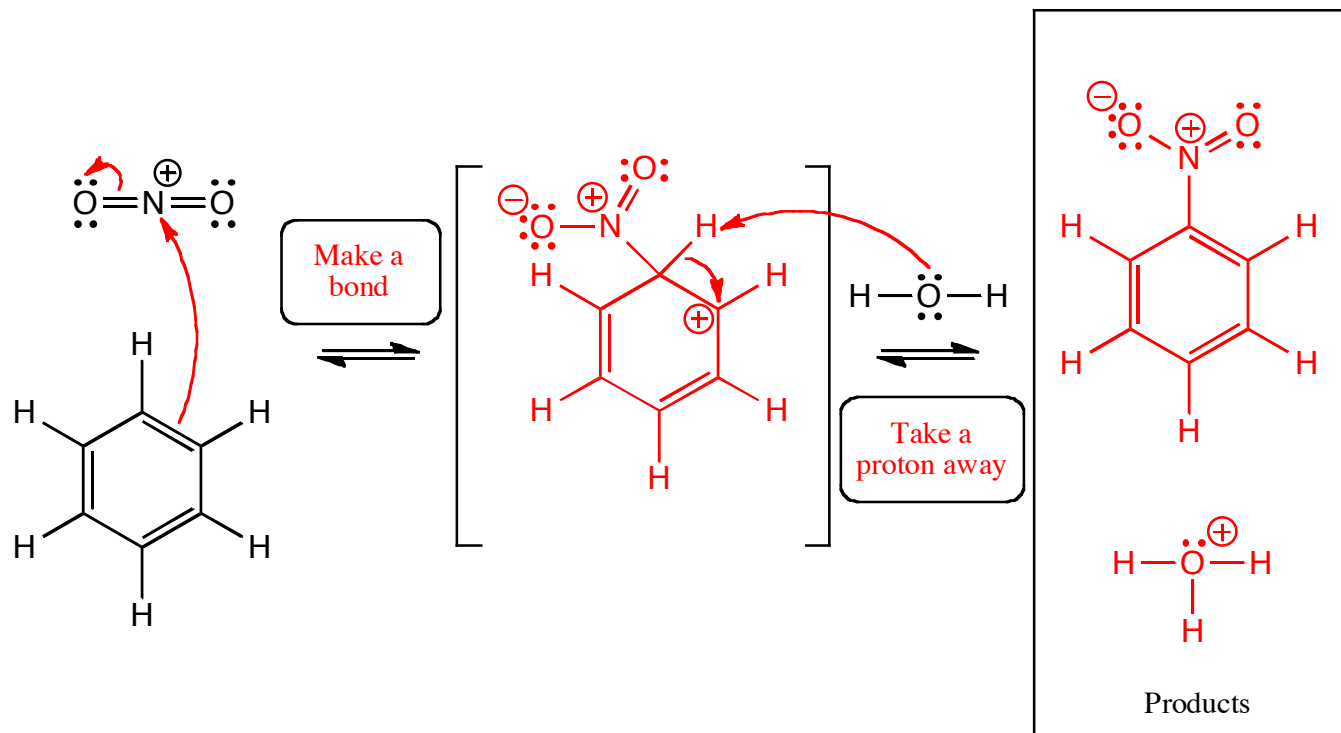
10. (2 pts each) In each of the boxes over an arrow, write the minimum number of equivalents of the specified reagent required to carry out the reaction shown **to completion**. If only a catalytic amount is needed, write "CAT". Note: **You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent.**



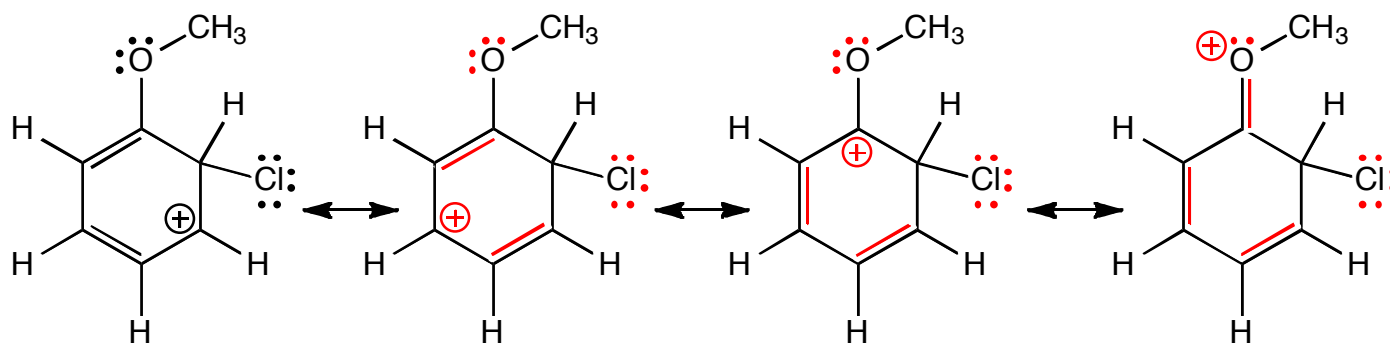
11. (26 pts) Complete the mechanism for the following Michael reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR THE PRODUCTS, MARK IT WITH AN ASTERISK AND LABEL AS "RACEMIC" IF RELEVANT. IN THE BOX BY EACH SET OF ARROWS, WRITE WHICH OF THE 4 MECHANISTIC ELEMENTS IS INDICATED IN EACH STEP OF YOUR MECHANISM (For example, "Add a proton").



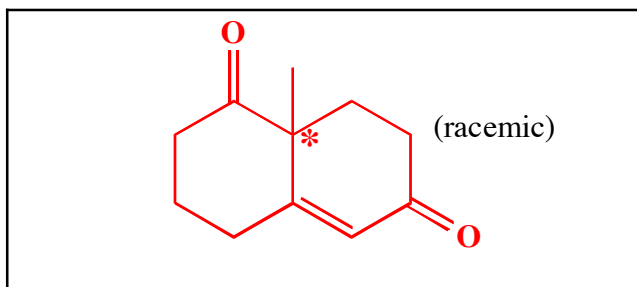
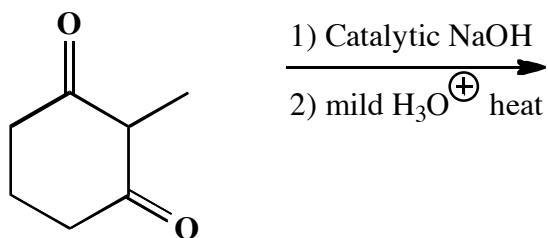
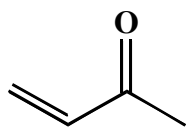
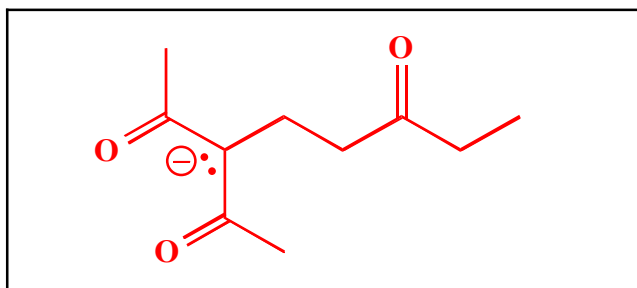
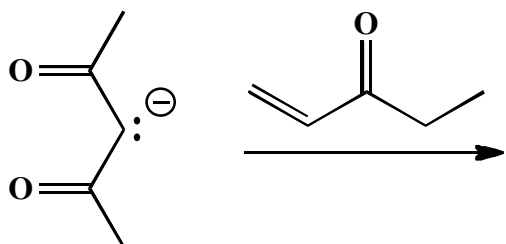
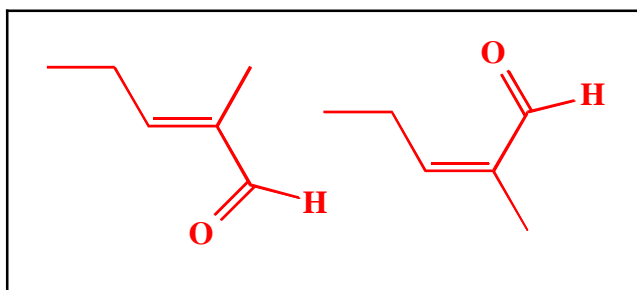
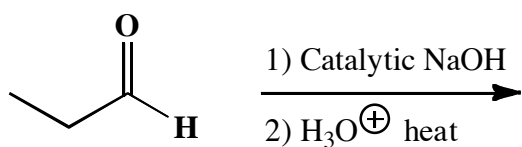
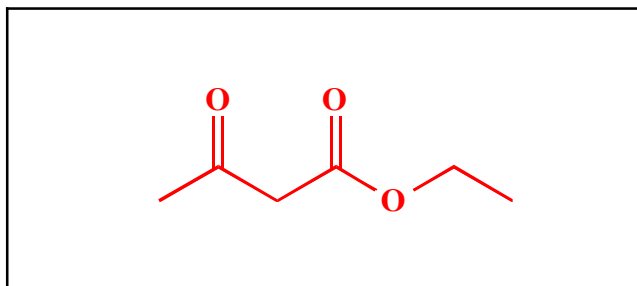
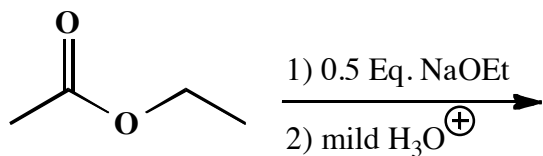
12. (11 pts) Complete the mechanism for the following electrophilic aromatic substitution reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR THE PRODUCTS, MARK IT WITH AN ASTERISK AND LABEL AS "RACEMIC" IF RELEVANT. IN THE BOX BY EACH SET OF ARROWS, WRITE WHICH OF THE 4 MECHANISTIC ELEMENTS IS INDICATED IN EACH STEP OF YOUR MECHANISM (For example, "Add a proton").



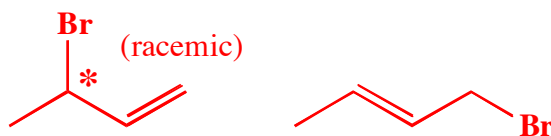
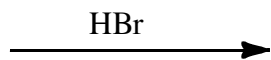
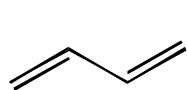
13. (9 pts) Complete the following by drawing the three most important contributing structures of the following arenium ion intermediate. Make sure to show all bonds, lone pairs and formal charges. You do not need to draw any arrows for this one.



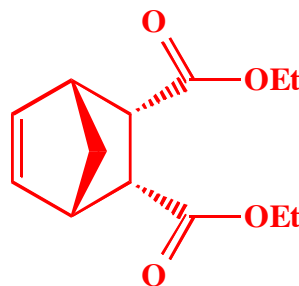
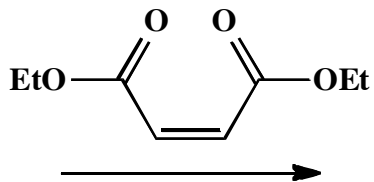
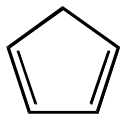
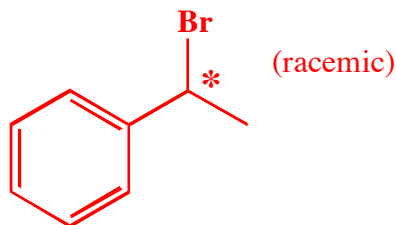
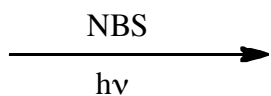
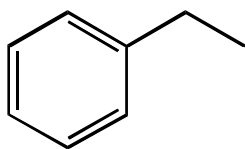
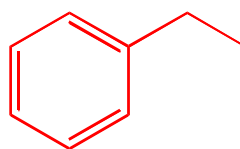
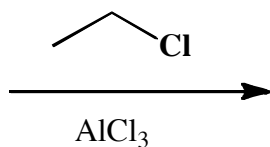
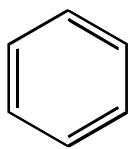
13. (3, 4 or 5 pts each) For the following reactions, draw the predominant product or products. When a new chiral center is created, mark it with an asterisk (\*) and if a racemic mixture is produced, you must write "racemic" under your structure. For an aldol reaction YOU NEED TO DEHYDRATE!!! If an E,Z mixture is produced as the result of the aldol dehydration step you have to draw both structures. These directions are different than you may have seen before. You should read them again so you know what we want.



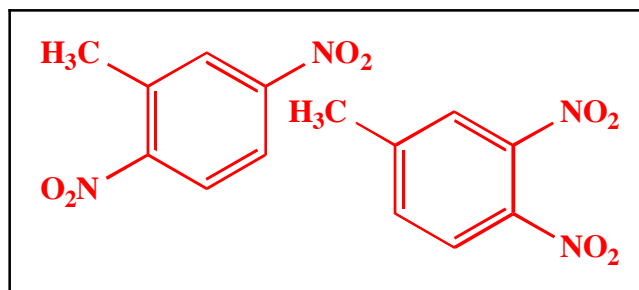
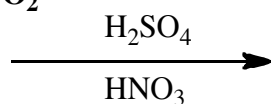
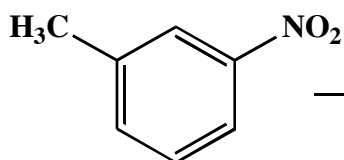
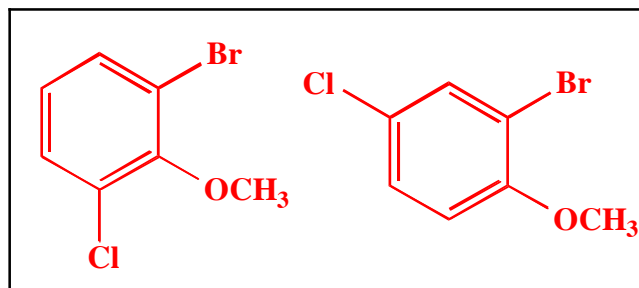
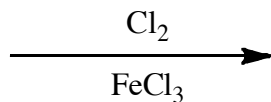
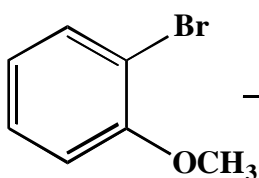
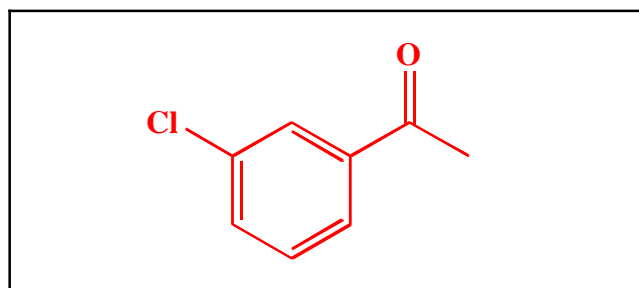
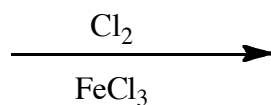
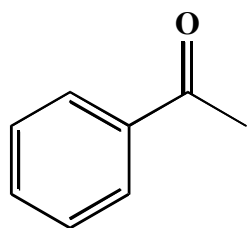
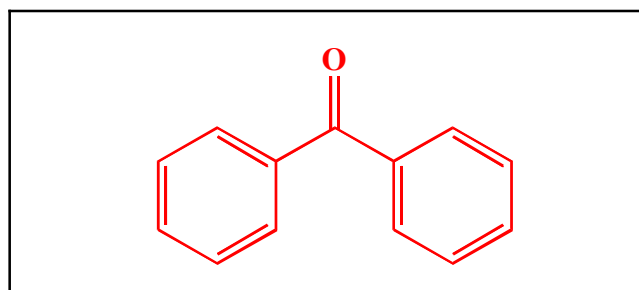
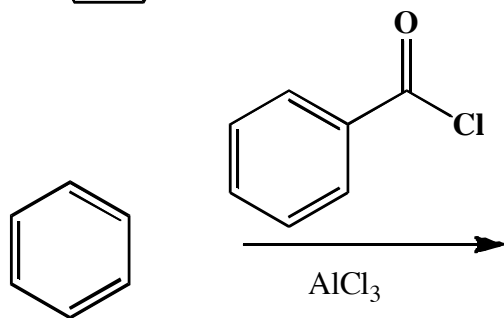
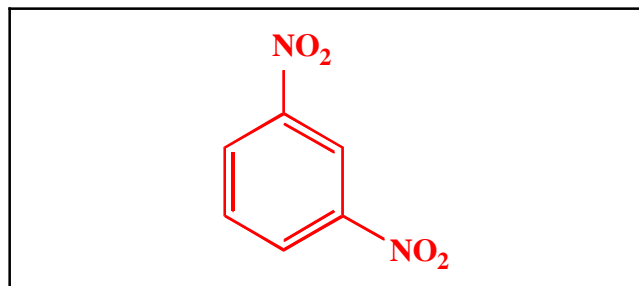
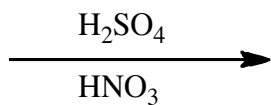
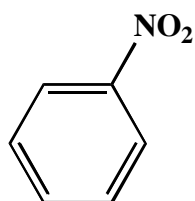
14. (3 or 5 pts each) For the following reactions, draw the predominant product or products. **When a new chiral center is created, mark it with an asterisk (\*) and if a racemic mixture is produced, you must write "racemic" under your structure. If both ortho and para products are produced, you need to draw both.** These directions are different than you may have seen before. You should read them again so you know what we want.



We are expecting two products

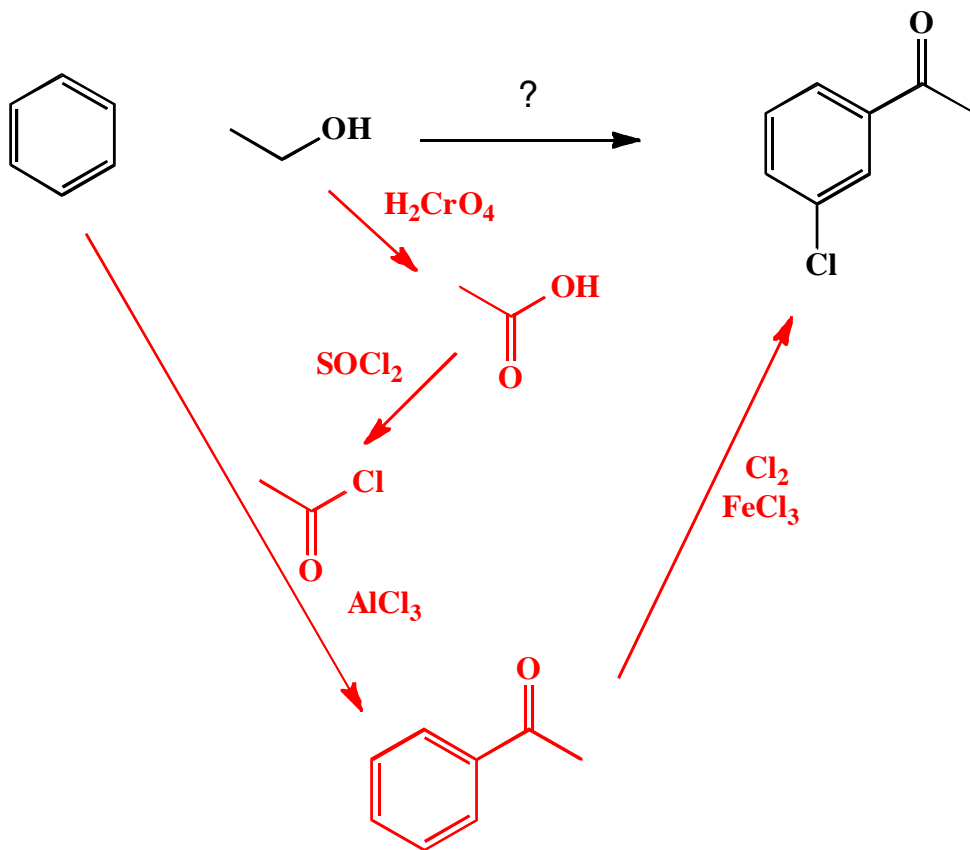


14. (3 or 5 pts each) For the following reactions, draw the predominant product or products. When a new chiral center is created, mark it with an asterisk (\*) and if a racemic mixture is produced, you must write "racemic" under your structure. If both ortho and para products are produced, you need to draw both. These directions are different than you may have seen before. You should read them again so you know what we want.



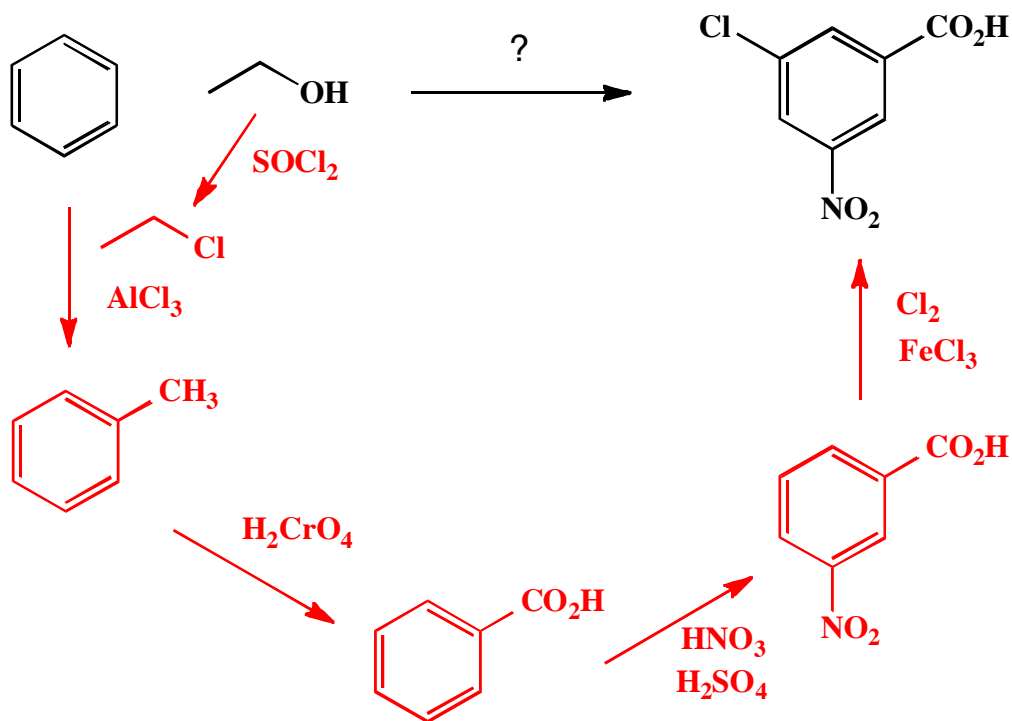
14. (10 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (\*) and make sure to right "Racemic" where appropriate. **Note that if a reaction gives both ortho and para products, you are allowed to isolate only one of these and move forward with your synthesis.**

Remember, all of the carbons of the product must come from the given starting materials.



14. (13 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (\*) and make sure to right "Racemic" where appropriate. **Note that if a reaction gives both ortho and para products, you are allowed to isolate only one of these and move forward with your synthesis.**

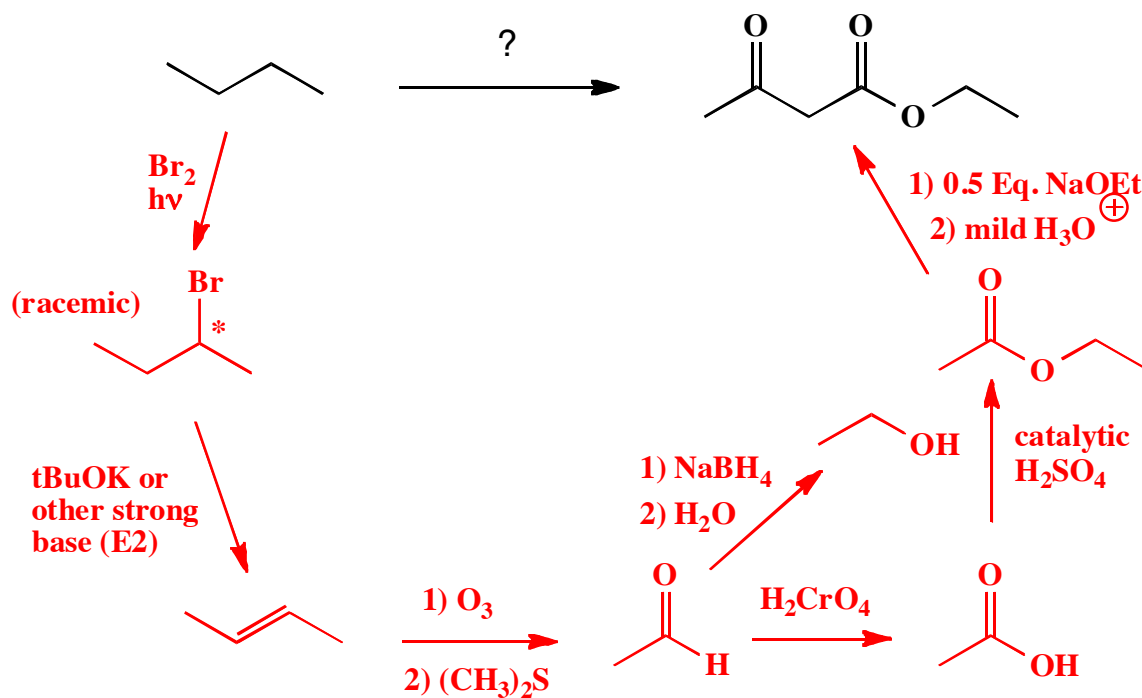
Remember, all of the carbons of the product must come from the given starting materials.





14. (19 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (\*) and make sure to right "Racemic" where appropriate.

Remember, all of the carbons of the product must come from the given starting material.



14. (9 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (\*) and make sure to right "Racemic" where appropriate.

Remember, all of the carbons of the product must come from the given starting material.

