## Practice Sets Organic Chemistry II Table of Contents

- Online Organic Chemistry II, Chem 360,
- Dr. Craig P. Jasperse, Minnesota State University Moorhead
- For full class website, see

• Fall/spring: https://collaborate.mnstate.edu/public/blogs/jasperse/online-organic-chemistry-courses/online-organic-chemistry-ii-360-fall-spring/

- Summer: <u>https://collaborate.mnstate.edu/public/blogs/jasperse/online-organic-chemistry-courses/online-organic-chemistry-ii-360-summer/</u>

   Second thttps://collaborate.mnstate.edu/public/blogs/jasperse/online-organic-chemistry-courses/online-organic-chemistry-ii-360-summer/
- Face: https://collaborate.mnstate.edu/public/blogs/jasperse/on-campus-chemistry-courses/organic-chemistry-ii-360/

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## Test 1 PS#1: Arrow-Pushing/Mechanisms Practice Set

Chem 360 Jasperse Name:

Arrow-Pushing Practice, Page 1:

- Draw arrows for each of the steps in the following reactions.
- I won't require this on tests, but you may find it useful to include all lone-pairs on atoms that react.

Due:

- <u>I won't require this on tests, but you may find it useful to draw in all hydrogens on atoms that</u> react. (It is not useful to draw in all H's on atoms that don't react.)
- Remember that <u>arrows track the movement of electrons</u>, so an arrow should go from the source of electrons and point directly to the atom that accepts them.



2. 
$$S_N^2$$
  $rac{}_{Br}$  + NaI  $rac{}_{I}$  + NaBr











For each of the following reactions, write whether the mechanism would be radical, cationic, or anionic?



## **Some Arrow-Pushing Guidelines**

- 1. Arrows follow electron movement.
- 2. Some rules for the appearance of arrows
  - The arrow must begin from the electron source. There are two sources:
    - a. An atom (which must have a lone pair to give)
    - b. A bond pair (an old bond that breaks)
  - An arrow must always point directly to an <u>atom</u>, because when electrons move, they always go to some new atom.
- 3. Ignore any Spectator Atoms. Any metal atom is always a "spectator"
  - When you have a metal spectator atom, realize that the non-metal next to it must have negative charge
- 4. Draw all H's on any Atom Whose Bonding Changes
- 5. Draw all lone-pairs on any Atom whose bonding changes
- 6. <u>**KEY ON BOND CHANGES**</u>. Any two-electron bond that changes (either made or broken) must have an arrow to illustrate:
  - where it came from (new bond made) or
  - an arrow showing where it goes to (old bond broken)

## 7. <u>Watch for Formal Charges and Changes in Formal Charge</u>

- If an atom's charge <u>gets more positive</u> ⇒ it's donating/losing an electron pair ⇒ <u>arrow must emanate from that atom or one of it's associated bonds</u>. There are two "more positive" transactions:
  - <u>When an anion becomes neutral</u>. In this case, an arrow will emanate from the atom. The atom has donated a lone pair which becomes a bond pair.
  - When a neutral atom becomes cationic. In this case, the atom will be losing a bond pair, so the arrow should emanate from the bond rather than from the atom.
- If an atom's charge <u>gets more negative</u> ⇒ it's accepting an electron pair ⇒ <u>an</u> <u>arrow must point to that atom</u>. Ordinarily the arrow will have started from a bond and will point to the atom.

#### 8. <u>When bonds change, but Formal Charge Doesn't Change, A "Substitution" is</u> <u>Involved</u>

- Often an atom gives up an old bond and replaces it with a new bond. This is "substitution".
- In this case, there will be an incoming arrow pointing directly at the atom (to illustrate formation of the new bond), and an outgoing arrow emanating from the old bond that breaks

### Test 1 PS#2: Acid Base Practice Set

Organic Chemistry Jasperse Acid-Base Practice Problems

# A. Identify each chemical as either an "acid" or a "base" in the following reactions, and identify "conjugate" relationships.

-You should have one acid and one base on each side

-You should have two conjugate pairs

1. 
$$CH_3CH_2OH + NaOH \longrightarrow CH_3CH_2ONa + H_2O$$
  
2.  $CH_3CH_2NHLi + CH_3OH \longrightarrow CH_3CH_2NH_2 + CH_3OLi$   
3.  $CH_3CH_2CO_2H + CH_3MgBr \longrightarrow CH_3CH_2CO_2MgBr + CH_4$   
4.  $CH_3OH + H_3O^+ \longrightarrow H_2O + CH_3OH_2^+$   
5.  $CH_3CH_2NH_3^+ + CH_3OH \longrightarrow CH_3CH_2NH_2 + CH_3OH_2^+$ 

B. Choose the More **Basic** for Each of the Following Pairs (Single Variable). You can use stability to decide.



## Test 1 PS#2: Acid Base Practice Set

#### C. Rank the basicity of the following sets: Multiple Variable Problems





E. Rank the acidity of the following sets: Multiple Variable Problems



F. Draw arrow to show whether equilibrium favors products or reactants. (Why?)



- G. For the following acid-base reaction,
  - a. put a box around the weakest base in the reaction
  - b. put a circle around the weakest acid
  - c. draw an arrow to show whether the equilibrium goes to the right or left. (4pt)

29.	∕OH	+	NHNa	ONa	+	∕NH <sub>2</sub>
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## Acid-Base Chemistry (Section 1.13-18)

A aidity/Pasiaity Tabla

Test 1 PS#2: Acid Base Practice Set

AU	ulty/Dasicity Tab						
Entry	Class	Structure	<u>Ka</u>	<u>Acid</u> Strength	Base	<u>Base</u> Strength	Base Stability
1	Strong Acids	H-Cl, H <sub>2</sub> SO <sub>4</sub>	10 <sup>2</sup>	1	CI <sup>⊖</sup> , HO−S−O 0 0		1
2	Hydronium	H <sub>3</sub> O <sup>+</sup> , ROH <sup>+</sup> cationic	10 <sup>0</sup>		H <sub>2</sub> O, HOR neutral		
3	Carboxylic Acid	R OH	10-5		R↓0⊖		
4	Ammonium Ion (Charged)	$ \begin{array}{c} R, +, H\\ R^{\ N} R \end{array} $ Charged, but only weakly acidic!	10 <sup>-12</sup>		$ \begin{array}{c} R \\ N \\ R^{\bullet} R \\ \text{Neutral, but basic!} \end{array} $		
5	Water	НОН	10 <sup>-16</sup>		<sub>но</sub> Ө		
6	Alcohol	ROH	10 <sup>-17</sup>		RO <sup>Ө</sup>		
7	Ketones and Aldehydes	O L a H	10 <sup>-20</sup>		O C C		
8	Amine (N-H)	(iPr) <sub>2</sub> N-H	10 <sup>-33</sup>		$(iPr)_2 N^{\ominus} Li^{\oplus}$		
9	Alkane (C-H)	RCH <sub>3</sub>	10 <sup>-50</sup>				

#### Quick Checklist of Acid/Base Factors

1. Charge

1. Cations more acidic than neutrals; anions more basic than neutrals

- 2. Electronegativity 3. Resonance/Conjugation
- 2. Carbanions < nitrogen anions < oxyanione < halides in stability
- 3. resonance anions more stable than anions without resonance
- When neutral acids are involved, it's best to draw the conjugate anionic bases, and then think from the anion stability side.
- The above three factors will be needed this semester. The following three will also ٠ become important in Organic II.
- 4. Hybridization

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- 5. Impact of Electron Donors/Withdrawers
- 6. Amines/Ammoniums

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Organic Chemistry 2 Jasperse

Test 1, Alcohol Chemistry

Draw Mechanisms for the Following Reactions



Test 1 PS#3: Alcohol-related Mechanisms Problems











Test 1 PS#3: Alcohol-related Mechanisms Problems









Test 1 PS#3: Alcohol-related Mechanisms Problems













More Retrosynthesis Problems: One of the students asked if I could generate















Harder Ones (more than one Grignard reaction required)







#### **Jasperse Organic II NMR Problems**

This practice-set collection includes only the first 10 or 42 practice 1.  $C_3H_7Cl$ NMR problems. For several reasons: 1. The full 42 are already included within the "all notes" collection. 2. Including the first 10 will give you a chance to re-practice those all on your own. (I'll do all of the first ten within class, too...) 3. 10 pages worth will match the number of pages in the answer key document; this way the documents will match up in terms of page numbers. 4. To print off the full set of 42 NMR practice problems, use this link: http://web.mnstate.edu/jasperse/Chem360/Classbook%20360/NMR%20Problems.pdf 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 28.09 43.44 ~~ ~~

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5.  $C_5H_{10}O_2$ 

Test 2 NMR: Jasperse NMR Problems





7.  $C_6H_{12}O_2$ 

Test 2 NMR: Jasperse NMR Problems





Test 2 NMR: Jasperse NMR Problems





10.Predict the Spectrum for: Test 2 NMR: Jasperse NMR Problems





c. Identify the Structure from the Shorthand NMR (nongraphic)

#### $C_4H_8O$

- 1.05, triplet, 3H
- 2.13, singlet, 3H
- 2.47, quartet, 2H

This practice-set collection includes only the first 10 or 42 practice NMR problems. For several reasons:

The full 42 are already included within the "all notes" collection.
 Including the first 10 will give you a chance to re-practice those all

on your own. (I'll do all of the first ten within class, too...)

3. 10 pages worth will match the number of pages in the answer key document; this way the documents will match up in terms of page numbers.

4. To print off the full set of 42 NMR practice problems, use this link:

Some Practice Problems for the Carbonyls Test 3 Draw the Products and Mechanisms for the following Reactions







9. 
$$\overset{OH}{\overset{H}}_{H}$$
  $\overset{H_2O, H^{\oplus}}{\overset{H}{\longrightarrow}}$   $\overset{O}{\overset{H}}_{H}$ 















Test 3 PS#1: Mechanism Practice (Many)

























heat



NaOEt EtOH heat





44. O H NaOMe MeOH

Some Practice Problems for the Carbonyls Test 3 RETROSYNTHESIS PRACTICE: Design synthesis for the following, FROM ALCOHOLS WITH NO MORE THAN 5 CARBONS. YOU MAY ALSO USE ESTERS, or any inorganic agents (PPh<sub>3</sub>, PBr<sub>3</sub>, PCC, H2CrO4, etc.)



No other alkene structural isomers allowed (in other words, don't make an alcohol elimination reaction)











## Test 3 PS#2: Retrosynthesis + Synthesis Design Practice

SYNTHESIS DESIGN PRACTICE: Provide Reagents for the Following Transformations. You may use anything you like, so long as you involve the starting chemical specified.



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Organic Chemistry Jasperse Acid-Base Practice Problems

# A. Identify each chemical as either an "acid" or a "base" in the following reactions, and identify "conjugate" relationships.

-You should have one acid and one base on each side

-You should have two conjugate pairs

1. 
$$CH_3CH_2OH + NaOH \longrightarrow CH_3CH_2ONa + H_2O$$
  
2.  $CH_3CH_2NHLi + CH_3OH \longrightarrow CH_3CH_2NH_2 + CH_3OLi$   
3.  $CH_3CH_2CO_2H + CH_3MgBr \longrightarrow CH_3CH_2CO_2MgBr + CH_4$   
4.  $CH_3OH + H_3O^+ \longrightarrow H_2O + CH_3OH_2^+$   
5.  $CH_3CH_2NH_3^+ + CH_3OH \longrightarrow CH_3CH_2NH_2 + CH_3OH_2^+$ 

B. Choose the More **Basic** for Each of the Following Pairs (Single Variable). You can use stability to decide.



## Test 4 PS#1: Acid-Base Practice (Easy)

#### C. Rank the basicity of the following sets: Multiple Variable Problems



D. Choose the More Acidic for Each of the Following Pairs: Single Variable Problems



Test 4 PS#1: <u>Acid-Base Practice (Easy)</u>

E. Rank the acidity of the following sets: Multiple Variable Problems



F. Draw arrow to show whether equilibrium favors products or reactants. (Why?)



- G. For the following acid-base reaction,
  - a. put a box around the weakest base in the reaction
  - b. put a circle around the weakest acid
  - c. draw an arrow to show whether the equilibrium goes to the right or left. (4pt)

29.	∕OH	+	NHNa	ONa	+	∕NH <sub>2</sub>
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## Acid-Base Chemistry (Section 1.13-18)

A aidity/Dagiaity Table

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Entry	<u>Class</u>	Structure	<u>Ka</u>	<u>Acid</u> Strength	Base	<u>Base</u> Strength	Base Stability
1	Strong Acids	H-Cl, H <sub>2</sub> SO <sub>4</sub>	10 <sup>2</sup>	ſ	Cl <sup>⊖</sup> , HO−S−O B		1
2	Hydronium	H <sub>3</sub> O <sup>+</sup> , ROH <sup>+</sup> cationic	10 <sup>0</sup>		H <sub>2</sub> O, HOR neutral		
3	Carboxylic Acid	R OH	10-5		R <sup>↓</sup> 0⊖		
4	Ammonium Ion (Charged)	R H R R H R R R Charged, but only weakly acidic!	10 <sup>-12</sup>		$ \begin{array}{c} R \\ N \\ R^{\prime} \\ \hline R \\ \hline N \\ Neutral, but basic! \end{array} $		
5	Water	НОН	10 <sup>-16</sup>		<sub>но</sub> Ө		
6	Alcohol	ROH	10 <sup>-17</sup>		RO <sup>⊖</sup>		
7	Ketones and Aldehydes	Ομαμ	10 <sup>-20</sup>		o a o		
8	Amine (N-H)	(iPr) <sub>2</sub> N-H	10-33		$(iPr)_2 N^{\bigcirc} Li^{\oplus}$		
9	Alkane (C-H)	RCH <sub>3</sub>	10-50				

#### Quick Checklist of Acid/Base Factors

1. Charge

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- 2. Electronegativity 3. Resonance/Conjugation
- 2. Carbanions < nitrogen anions < oxyanione < halides in stability 3. resonance anions more stable than anions without resonance
- - When neutral acids are involved, it's best to draw the conjugate anionic bases, and then think from the anion stability side.
- The above three factors will be needed this semester. The following three will also ٠ become important in Organic II.
- 4. Hybridization
- 5. Impact of Electron Donors/Withdrawers
- 6. Amines/Ammoniums

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	Test 4 PS#2:       Acid-Base Practice (Less Easy)         1								
Or	ganic Chemistry	II Jasperse	Acid-Base P	Practice Problems					
<u>A.</u>	A. Rank the basicity of the following sets: Multiple Variable Problems								
1.	CH <sub>3</sub> MgBr	CH <sub>3</sub> NHNa	CH <sub>3</sub> NH <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> NH					
2.	$\sim_{0}^{\ominus}$		∕ОН	CH <sub>3</sub> NH <sub>2</sub>					
3.	ONa	NHNa	ОН	ONa O					
4.	, O O	⊖ NH	ОН						
5.	CH <sub>3</sub> NHNa	CH <sub>3</sub> C(O)NH <sub>2</sub>	(CH <sub>3</sub> ) <sub>3</sub> N	pyridine					
6.	(CH <sub>3</sub> ) <sub>3</sub> N	pyridine	CH <sub>3</sub> NH <sub>2</sub>	water					
7.	(CH <sub>3</sub> ) <sub>3</sub> N	PhCO <sub>2</sub> Na	CH <sub>3</sub> NH <sub>2</sub>	PhCH <sub>2</sub> ONa water					
8.	(CH <sub>3</sub> ) <sub>3</sub> N	4-methylaniline	aniline	pyrrole					
9.	methylamine	4-ethanoylanil	ine aniline	pyridine					
10.	CH <sub>3</sub> NH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> ONa	PhCO <sub>2</sub> Na	methanol					



c. Which will extract from ether into acid (HCl) water?



Some Practice Problems for the Amines/Acids Test 4 Draw the Mechanisms for the following Reactions Page 4 has some synthesis-design practice problems.

















Design Syntheses for the following transformations

