Chemistry 2030
"Introduction to Organic Chemistry"
Fall Semester 2014
Dr. Rainer Glaser

Examination #4
“Ether Cleavage & Epoxide Opening, Aldehydes & Ketones, Enols & Aldol Reaction, Carboxylic Acids & Carboxylic Acid Esters.”

Thursday, November 20, 2014, 8:25 - 9:15 am

Name:

Answer Key

| Question 1. Ether Chemistry: Ether Cleavage & Epoxide Opening Rxns. | 20 |
| Question 3. Aldehydes & Ketones II: Hydride Reductions, Rxns. with Carbanions (Grignards), Enols & Aldol Rxns. | 20 |
| Question 4. Carboxylic Acids: Nomenclature, Properties, Synthesis. | 20 |
| Question 5. Carboxylic Acid Esters: Nomenclature, Fischer Esterification, Lactones. | 20 |
| Total | 100 |

ALLOWED: Periodic System of the Elements (printed, w/o handwriting on it). Molecular models (you can bring pre-made models). Simple, non-programmable calculator (not really needed).

Question 1. Ether Chemistry. (20 points)

(a) Consider the reaction of ethyl isopropyl ether with HI. Provide abbreviated structural formulas for the two products formed and give their names. (6 points)

\[(\text{CH}_3\text{)}_2\text{CH–O–CH}_2\text{–CH}_3\ + \text{HI} \rightarrow (\text{CH}_3\text{)}_2\text{CH–OH} + \text{I–CH}_2\text{–CH}_3\]

isopropanol or 2-propanol  ethyl iodide or iodoethane

\[\text{SN}_2 \text{ at the primary carbon is faster than at the secondary carbon.}\]

\[(\text{CH}_3\text{)}_2\text{CH–O–CH}_2\text{–CH}_3\ + \text{HI} \rightarrow (\text{CH}_3\text{)}_2\text{CH–I} + \text{HO–CH}_2\text{–CH}_3\]

isopropyl iodide or 2-iodopropane  ethanol

Partial credit for this alternative cleavage.

(b) Consider the acid-catalyzed cleavage of ethylene oxide with 1-propanol. Provide abbreviated structural formulas for the protonated epoxide substrate, of the intermediate formed by addition of 1-propanol to the protonated epoxide, and of the final product. (6 points)

<table>
<thead>
<tr>
<th>Protonated Ethylene Oxide</th>
<th>Intermediate</th>
<th>Final Product</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Protonated Epoxide" /></td>
<td><img src="image2" alt="Intermediate" /></td>
<td><img src="image3" alt="Final Product" /></td>
</tr>
</tbody>
</table>

(c) Consider the acid-catalyzed cleavage of propylene oxide with 1-propanol. Provide an abbreviated structural formula of the final product. This reaction proceeds via an ______ (S\text{N}_1, S\text{N}_2) mechanism and the ______ (weak, strong) nucleophile propanol attacks the ______ (more, less) substituted carbon. (4 points)

![Propylene Oxide](image4)

(d) Consider the cleavage of propylene oxide with sodium propoxide in propanol. Provide an abbreviated structural formula of the final product. Propoxide is a ______ (weak, strong) nucleophile and the reaction proceeds via an ______ (S\text{N}_1, S\text{N}_2) mechanism and propoxide attacks the ______ (more, less) substituted carbon. (4 points)

![Propylene Oxide](image5)
Question 2. Aldehydes & Ketones I. (20 points)

(a) Provide abbreviated structural formulas of the substrate and of the final product of the hydration of 1-pentyne using proton and Hg$^{2+}$ catalysis. Provide two acceptable names for the product. (4 points)

Substrate: H$_3$C−(CH$_2$)$_2$−C≡C−H  
Product: H$_3$C−(CH$_2$)$_2$−CO−CH$_3$

Names of Product: Methyl propyl ketone and 2-pentanone

(b) Consider the reaction of benzaldehyde with ethylmagnesium bromide. Provide the structures of benzaldehyde, of the initial addition product (an alkoxide), and of the product formed after hydrolysis. This reaction exemplifies the general approach for the synthesis of a ____________ (primary, secondary, tertiary) alcohol by reaction of a(n) ____________ (aldehyde, ketone) with a Grignard reagent and subsequent hydrolysis. (6 points)

(c) Draw the structures of the products formed by the reaction of acetone, (H$_3$C)$_2$C=O with the indicated reagents. In each case, write down the name of the class of compounds to which the product belongs. The box on the top-left serves as an example. (10 points)
Question 3. Aldehydes & Ketones II. (20 points)

(a) Butanal (H₃C−CH₂−CH₂−CH=O) is an enolizable aldehyde. Draw the two important resonance forms of the enolate formed by deprotonation of butanal at the ____ (α, β, γ) carbon. Show all lone pairs and formal charges; use the correct resonance arrow. Use curved arrows to show the electron flow that converts one resonance forms into the other. (6 points)

(b) On the left, draw the structure of the product of the base-catalyzed aldol reaction of butanal, the butanal aldol. Heating of an aldol leads to dehydration. On the right, draw the structure of the dehydration product of butanal aldol. (8 points)

(c) Provide the structure of the mosquito repellent 2-ethylhexane-1,3-diol (a.k.a. “6-12”) in the box on the right. This pesticide can be prepared in two steps from butanal. The first reaction is a base-catalyzed aldol reaction to form butanal aldol. The second reaction is a __hydrogenation__ of butanal aldol and requires a catalyst such as __nickel__ (or other metal). (4 points)

(d) Consider the reduction of H₂C=CH−CH=O with LiAlH₄ followed by hydrolysis. Draw the structure of the final product. (2 points)
Question 4. Carboxylic Acids. (20 points)

(a) Propionic Acid is the trivial name for the carboxylic acid with _3_ carbon atoms, and its systematic IUPAC name is **propanoic** acid. Butanedioic Acid is the systematic IUPAC name for the dicarboxylic acid with _4_ carbon atoms, and its common name is **succinic** acid. Draw their complete structures. (6 p.)

(b) The electrostatic potential (ESP) surface plot is shown of acetic acid, H₃C-COOH. Draw a complete structure of acetic acid. Your structure drawing should be aligned as much as possible with the orientation of the molecules in the ESP plot. In your structure drawing, draw a SQUARE around the hydrogen bond donor and draw a CIRCLE around the best hydrogen bond acceptor. Finally, provide the two most important resonance forms of acetate ion. (6 points)

(c) Syntheses of Carboxylic Acids. Provide substrate, reagent or product as requested. (8 points)

Consider the oxidation of toluene with hot KMnO₄. Show substrate and product.

Consider the conversion of 2-bromopropane (H₃C)₂CHBr to (H₃C)₂CH–COOH. Show the reaction intermediates and provide the reagents (1) for the Grignard formation, (2) for the reaction of the Grignard compound, and (3) for the workup that gives the neutral acid.
Question 5. Carboxylic Acid Esters. (20 points)

(a) γ-Hydroxybutyric acid (GHB), a.k.a. “Lollipops”, “Liquid Ecstasy”, “Liquid X”, “Liquid G”, and “Fantasy”, is one of the three most common date rape drugs. GHB is easily made from γ-butyrolactone (GBL). Draw the complete structural formulas of GHB and GHL. (6 points)

(b) Propyl acetate \( \text{H}_3\text{C}–\text{CO}–\text{O}–\text{CH}_2–\text{CH}_2–\text{CH}_3 \) can be made by Fischer esterification of the carboxylic acid _____________ (formic acid, acetic acid, propanoic acid, benzoic acid) and the alcohol _____________ (methanol, ethanol, propanol, phenol). Consider the mechanism of propyl acetate formation by Fischer esterification (catalyzed by a strong mineral acid). Draw the structural formulas of the species indicated (show all lone pairs and formal charges). You may abbreviate the methyl group as “\( \text{H}_3\text{C}– \)” or as “Me–” and the propyl group as “\( \text{H}_7\text{C}_3– \)” or as “Pr–”. (14 points)