

# Chemistry 212 — Fall Semester 1996 Examination #2

University of Missouri—Columbia

Prof. Rainer Glaser

Wednesday, October 16, 1996

103 Schlundt Hall, 8:40 - 9:30

*featuring*  
*Carboxylic Acids and Carboxylic Acid Derivatives.*  
*Preparations, Properties & Reactions.*

Your Name:

**Herr Dr. Rainer Glaser**

	Max.	Yours
Question 1 (Properties)	20	
Question 2 (Fats & Soaps)	30	
Question 3 (Reactions)	30	
Question 4 (Reductions)	20	
Total	100	



**Do not turn the page until advised to do so.**



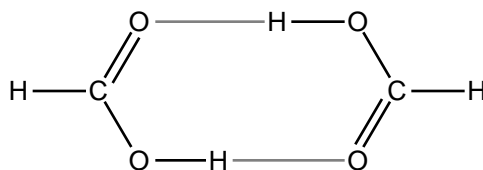
**Question 1.** Things Characteristic of Carboxylic Acids: Structure, Acidity & Spectroscopy. (20 points)

Formic acid, **HCOOH**, also known as methanoic acid in the IUPAC nomenclature, is the simplest carboxylic acid. Considering HCOOH, let us review a few properties of carboxylic acids.

**(a) Boiling Points.** The molecular mass of HCOOH is 46 and very close to the molecular mass of 44 of propane. Despite the similar mass, the boiling points of propane and formic acid differ drastically: Propane is a gas at room temperature and its boiling point is  $-42.1^{\circ}\text{C}$ . Formic acid is a liquid at room temperature and it boils at  $+100.6^{\circ}\text{C}$ ! The high boiling point of formic acid is due to aggregation in liquid phase as the result of strong hydrogen-bonding between the negatively (positively, negatively) charged acceptor and the highly acidic (acidic, basic, neutral) hydroxyl-hydrogen of the carboxy group. Draw the structure of the formic acid aggregate present in solution. Note that the boiling

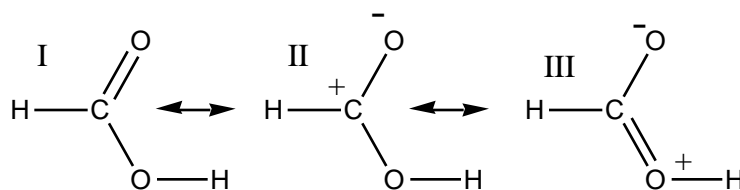
points of formic acid and of water are just about equal! Water has a molecular mass of only 18, less than half the molecular mass of HCOOH. Methane is the respective hydrocarbon with the same mass as water and  $\text{CH}_4$  has a boiling point of  $-161.7^{\circ}\text{C}$ . From these data, one can conclude that aggregation of water is more (more, less) important as compared to aggregation of formic acid.

**Structure of Aggregate:**



**(b) Acidity of Carboxylic Acids.** The  $\text{pK}_a$  value of acetic acid is a good number to remember as a reference and you do know that the value is +4.75 (give value with sign). The acidity of formic acid was not mentioned in the lecture. However, considering the electron-donating (donating, withdrawing) ability of the methyl group, it is clear that the acidity of HCOOH is higher (lower, equal, higher) compared to acetic acid and among the  $\text{pK}_a$  values of 3.75, 4.75, and 5.75 we can choose with confidence the value of 3.75 as the  $\text{pK}_a$  of formic acid.

**(c) The  $^1\text{H-NMR}$  Spectroscopy of HCOOH.** The underlined hydrogen H-COOH shows a chemical shift of 8 ppm which is less than in formaldehyde. Thus, the H-COOH hydrogen is more (more, less) shielded compared to the H-CHO hydrogen. Explain using resonance forms.

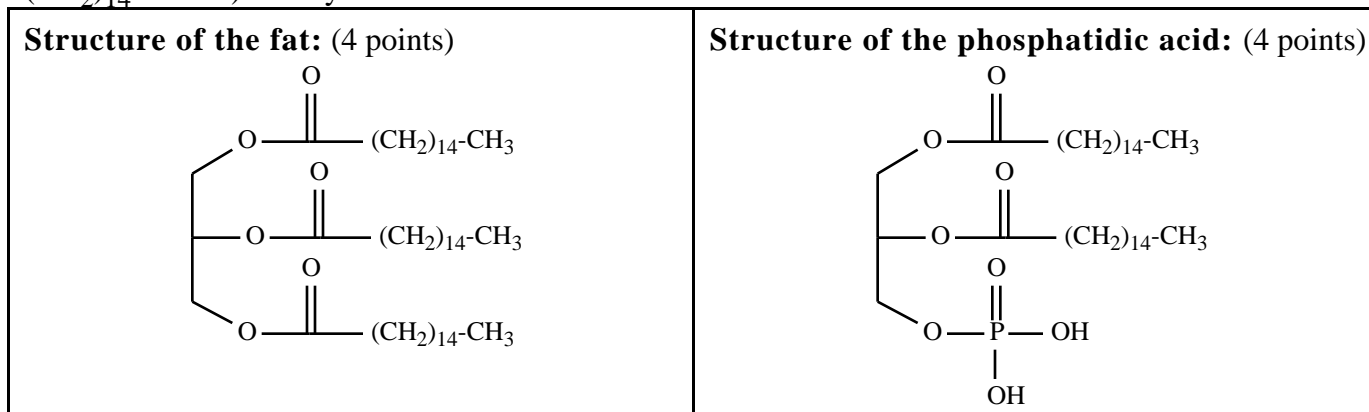


Hydroxyl-O donates to CO-carbon (III).

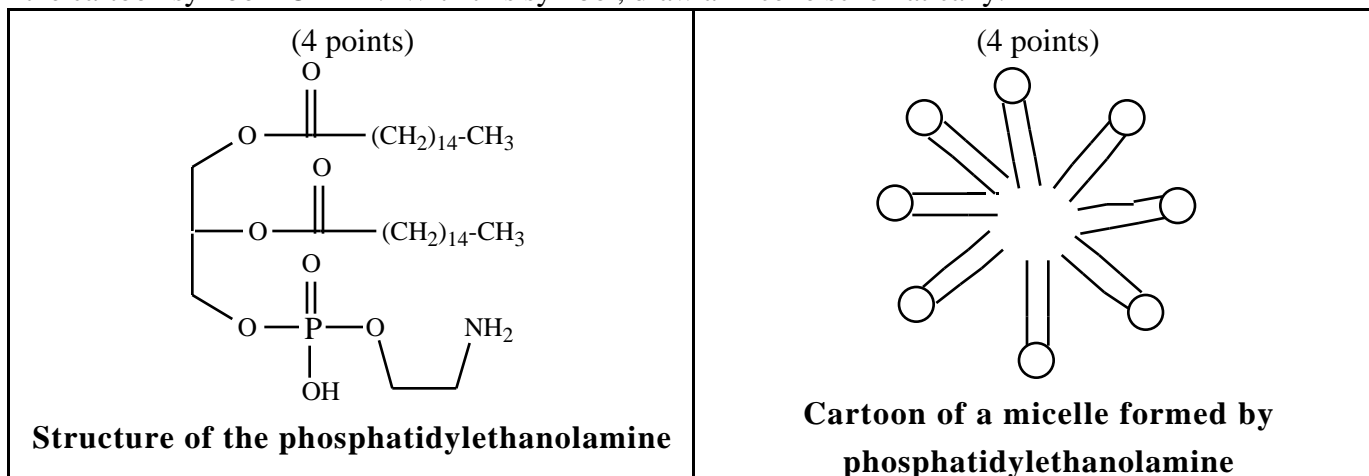
Lone pairs omitted (but you should have them drawn).

**Question 2.** Things to Aggregate in Spherical Clusters: Micelles of Lipids and Soaps. (20 points).

(a) **Fats** are esters of long-chain carboxylic acids (“fatty acids”) and glycerol (propane-1,2,3-triol). The polar ester functions are completely “buried” in the molecule and fats are therefore completely nonpolar when seen from the outside. Phospholipids contain two fatty acids and the third alcohol function of the triol is used to form an ester with phosphoric acid. The resulting monophosphate ester is called **phosphatidic acid**. Draw the structures of a fat and of a phosphatidic acid using palmitic acid ( $\text{H}_3\text{C}-(\text{CH}_2)_{14}-\text{COOH}$ ) as fatty acid.

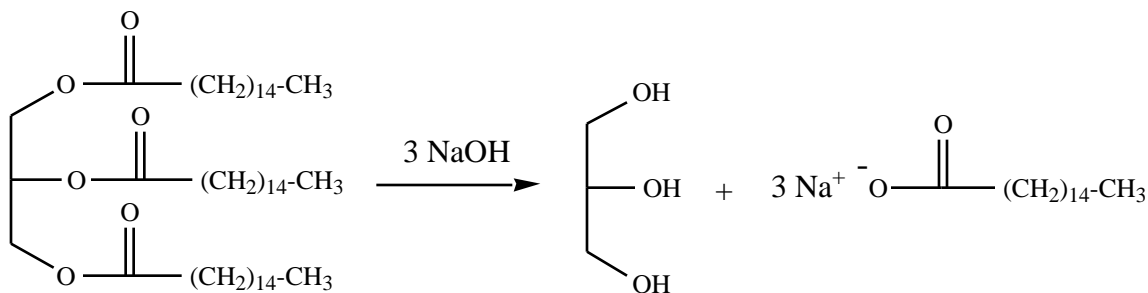


(b) Free phosphatidic acids are rare. Instead, the phosphoric acid moiety is usually esterified with another alcohol. The ester formed with the **phosphatidic acid** are the **phosphatidyl** derivatives. We learned about **phosphatidylcholine**, the ester of phosphatidic acid and choline. Now let’s look at a simpler case in which the phosphoric acid moiety is esterified with ethanolamine,  $\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ , to give **phosphatidylethanolamine**. Draw the structure of this compound. Phosphoglycerides are “**amphiphilic**”, which means they have polar and nonpolar fragments. There are two long non-polar “tails” and there is one very polar “head”. It is for this reason that we describe phosphoglycerides using the cartoon symbol “O===”. With this symbol, draw a micelle schematically.



**(c) Saponification (alkaline hydrolysis) of fats yields soaps.** Using sodium hydroxide as the base, give the reaction for the saponification of the fat discussed in part (a) — the fat containing palmitic acid ( $\text{H}_3\text{C}-(\text{CH}_2)_{14}-\text{COOH}$ ). Considering that palmitic acid is hexadecanoic acid, give the correct IUPAC name of the saponification product derived from the fatty acid.

**Saponification reaction with correct stoichiometry:** (3 points)

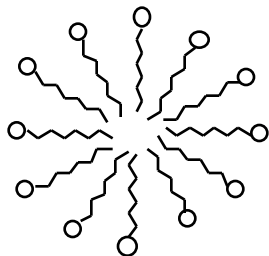


**IUPAC name of the soap:** (2 points)

Sodium hexadecanoate

**(d) The way soaps work.** Soaps are salts of fatty acids. Just like phosphoglycerides, the anions contained in soap are **amphiphilic** as they contain a polar head group and a non-polar tail. Hence, soap can form micelles just like phosphoglycerides and the only difference is that there are one (soap) or two (phosphoglycerides) tails per polar head group. On this background, explain how soap solubilizes fat.

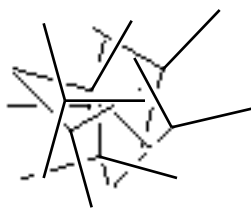
**Structure of soap in water (cartoon)**



(3 points)

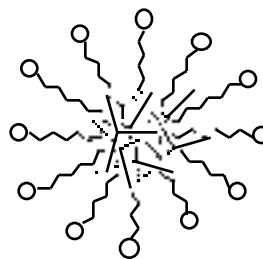
+

**Fat, insoluble in water**  
(Y symbolizes fat, three tails)

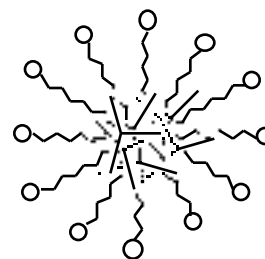


(3 points)

**Solution of grease in soap water**  
(cartoon)



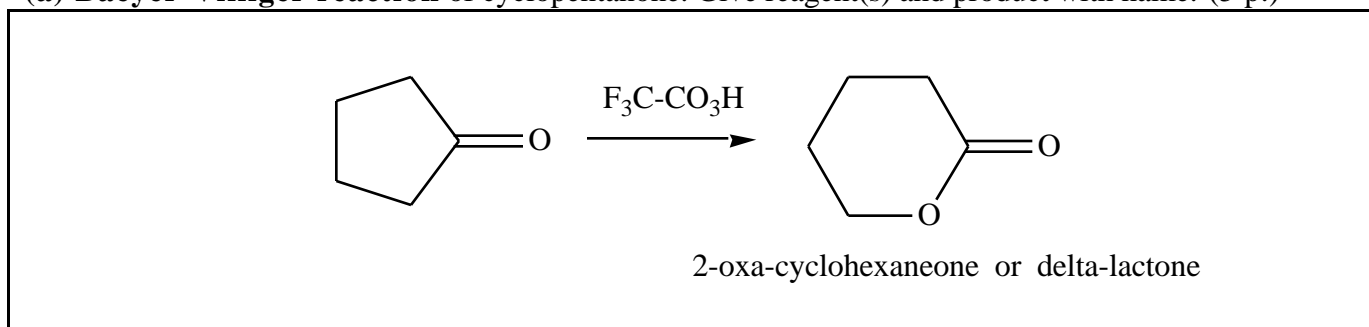
fat gets inside the soap micelles  
the fats are shown as “Y” (3 nonpolar tails)



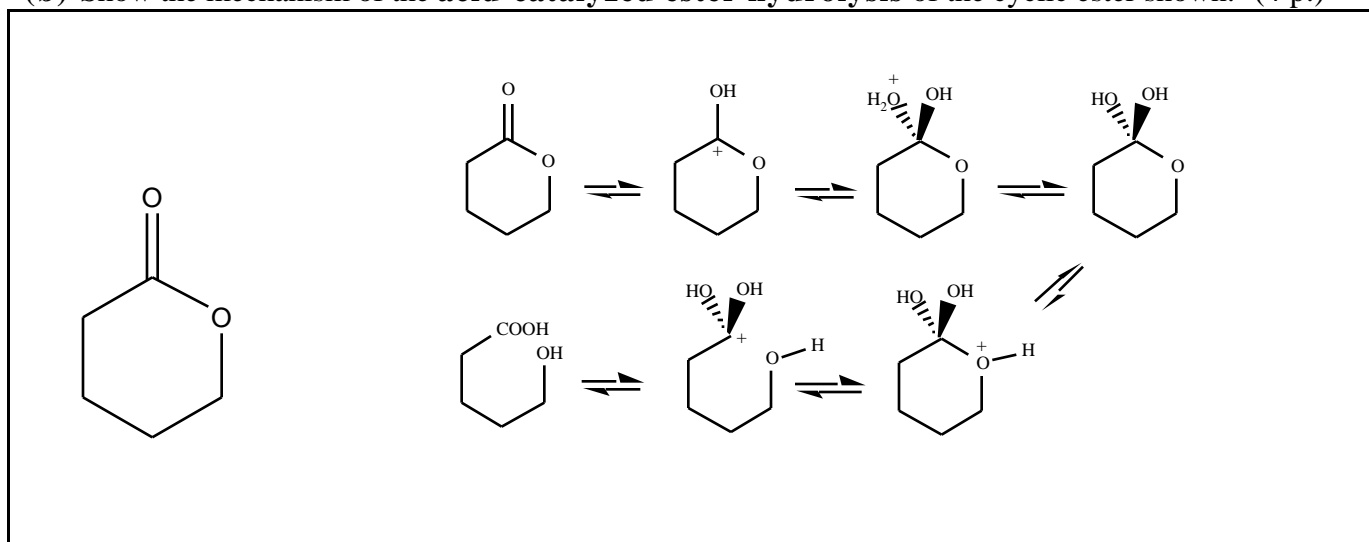
(3 points)

**Question 3.** Things to Transform: Functional Group Transformations. (30 points)

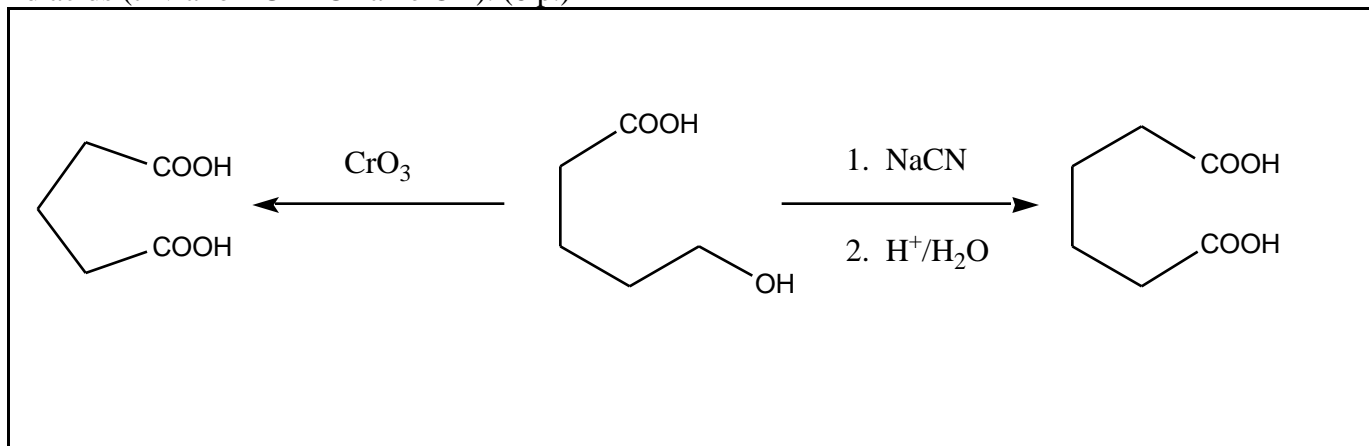
(a) **Baeyer-Villiger reaction** of cyclopentanone. Give reagent(s) and product with name. (5 p.)



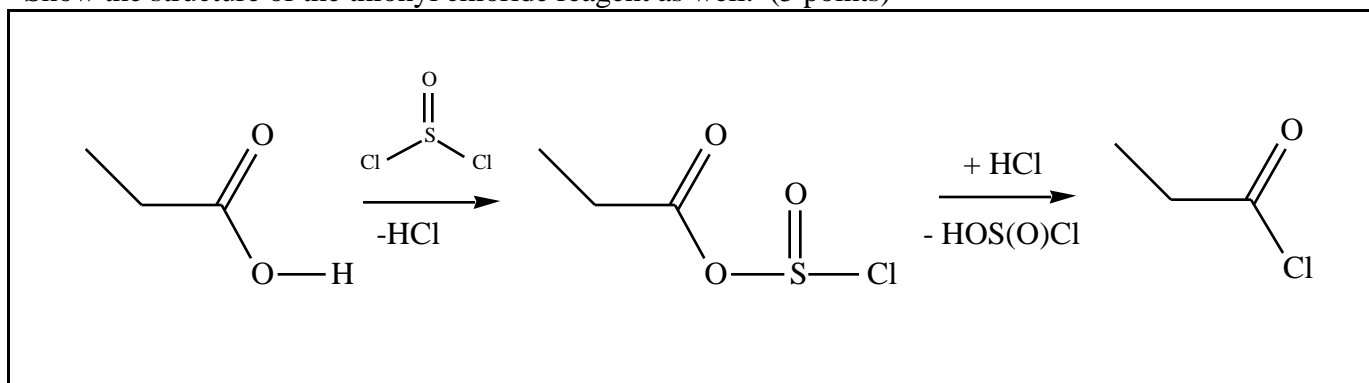
(b) Show the mechanism of the **acid-catalyzed ester hydrolysis** of the cyclic ester shown. (4 p.)



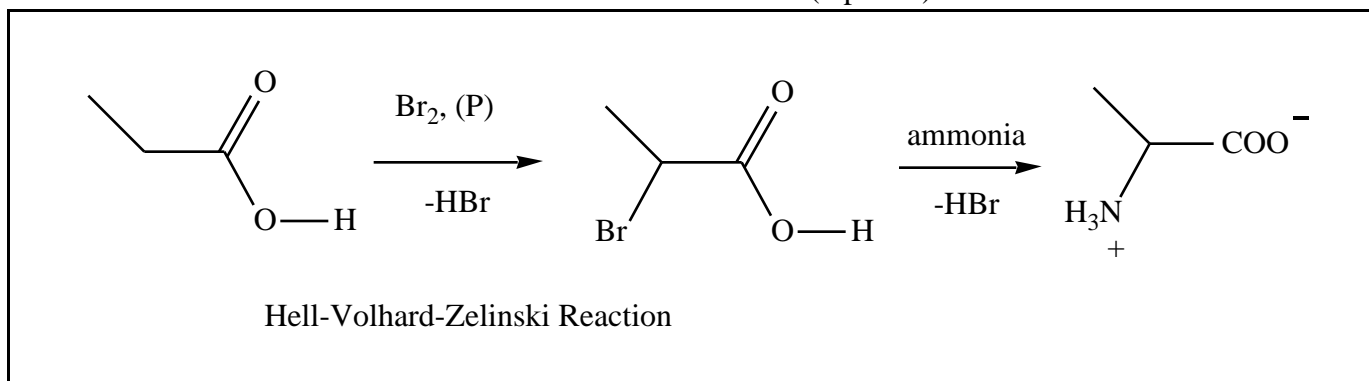
(c) Suggest reagents to transform the hydroxy-substituted acid into the **two diacids** shown. Name the diacids (trivial or IUPAC name OK). (6 p.)



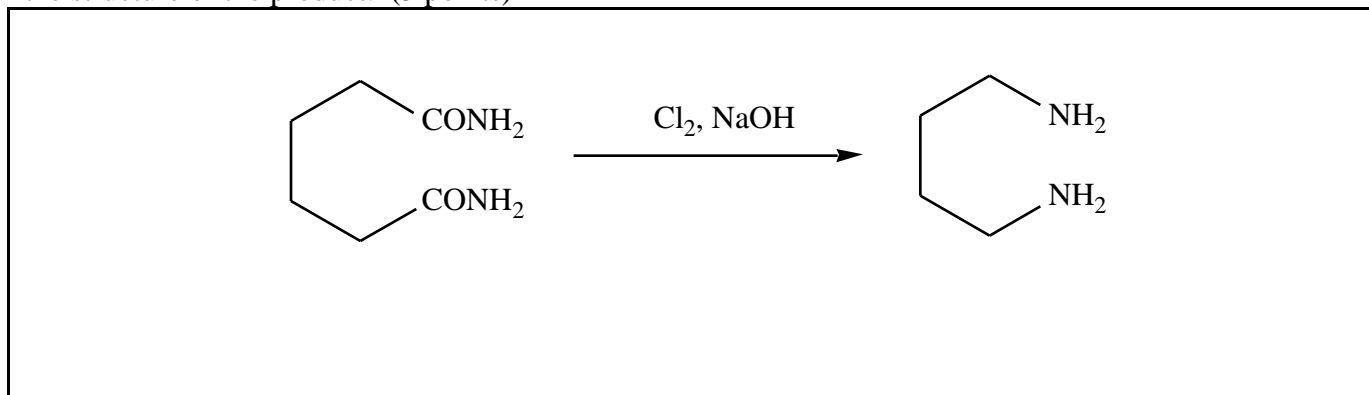
(d) Prepare **propanoylchloride** from the appropriate carboxylic acid and thionyl chloride. Draw the structures of the carboxylic acid, of the intermediate inorganic ester, and of the propanoylchloride product. Show the structure of the thionyl chloride reagent as well. (5 points)



(e) Starting from propanoic acid, suggest a synthesis of the respective  $\alpha$ -**aminoacid**. For the reaction used to introduce the functionality into the  $\alpha$ -position, specify the reagents employed and give the name of this reaction. Draw the  $\alpha$ -aminoacid in its **zwitterion** form. (5 points)



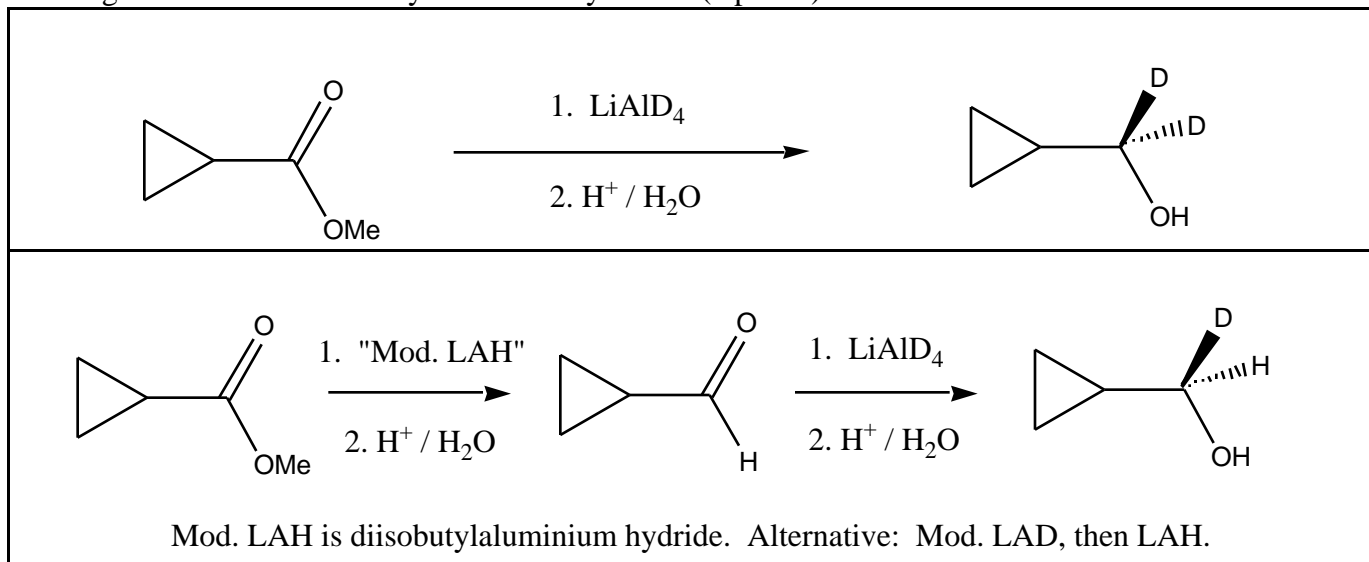
(f) The **diamide of adipic acid** is subjected to a **Hofmann rearrangement**. Give the structure of adipic acid diamide, specify the reagents employed to bring about the Hofmann rearrangement, and give the structure of the product. (5 points)



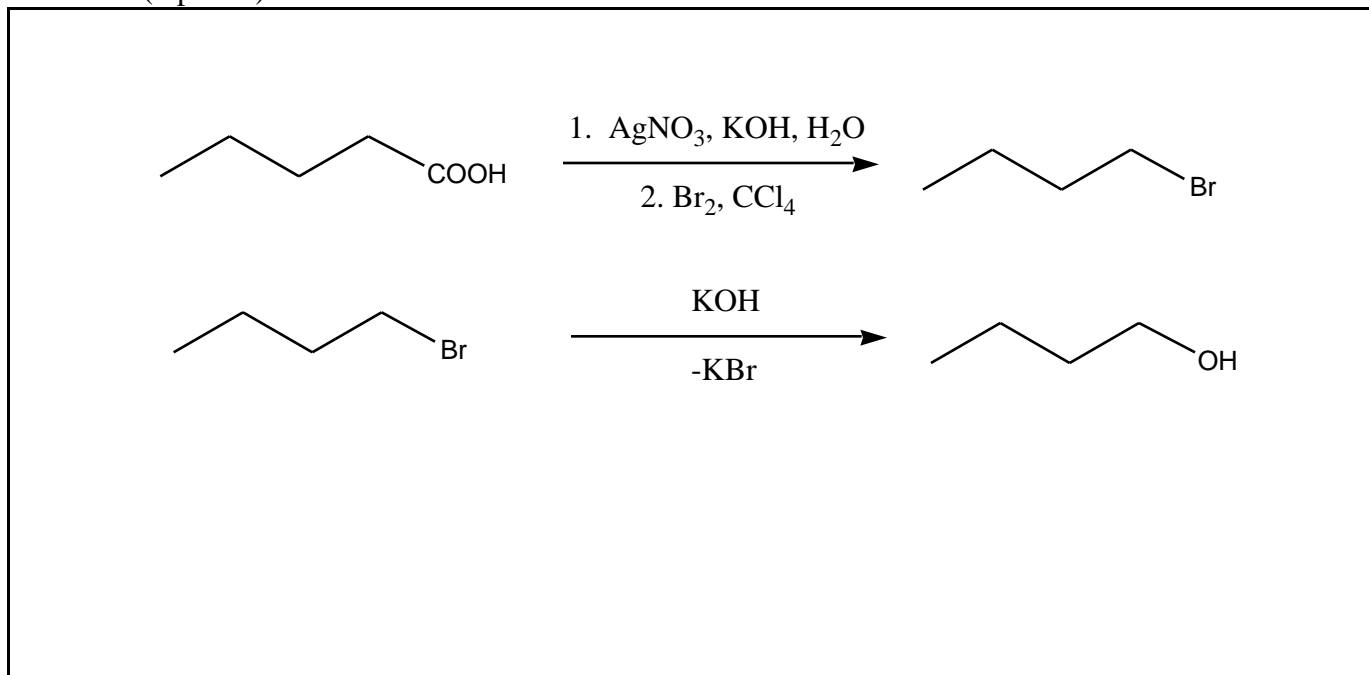
*Descartes: Je pense, alors je suis. Glaser: Just be!*

**Question 4.** Things to Reduce: Acid Derivatives to Carbonyls, Alcohols, and Amines. (20 points)

(a) Suggest a synthetic route to make the **dideuterated** and the **monodeuterated alcohols** shown starting from the **same** carboxylic acid methyl ester. (5 points)

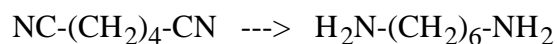


(b) The **Hunsdieker reaction** also can be seen as a reduction since this reaction can be used to convert an acid to an alcohol without having to use a “reducing reagent” and using in fact an “oxidizing reagent”! For the case of **pentanoic acid**, specify the reagents used to afford the Hunsdieker reaction and show the product of this reaction. Then specify the reagent(s) needed to convert the Hunsdieker product to an alcohol. (6 points)



(c) Suggest two ways to afford the reduction of 1,4-dicyanobutane to 1,6-diaminohexane. (4 points)

**Give overall reaction with structures:**



**Reagents for the first reduction method:**

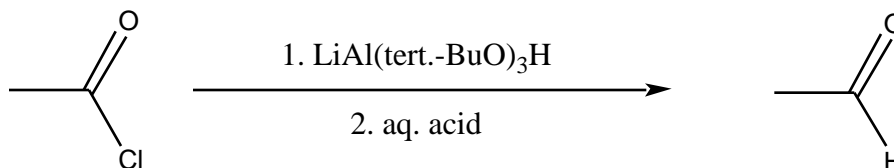
1. LAH 2. aq. acid

**Reagents for the other reduction method:**

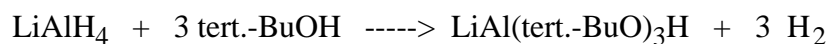
$\text{H}_2/\text{PdO}_2$

(d) Suggest a way to reduce **acetylchloride to acetaldehyde** with a modified LAH reagent. Give structures and overall reaction and specify the modified LAH reagent. Also show how this modified LAH reagent is made. (5 points)

**Reduce acetylchloride to acetaldehyde:**



**Preparation of the modified LAH reagent:**



The End

