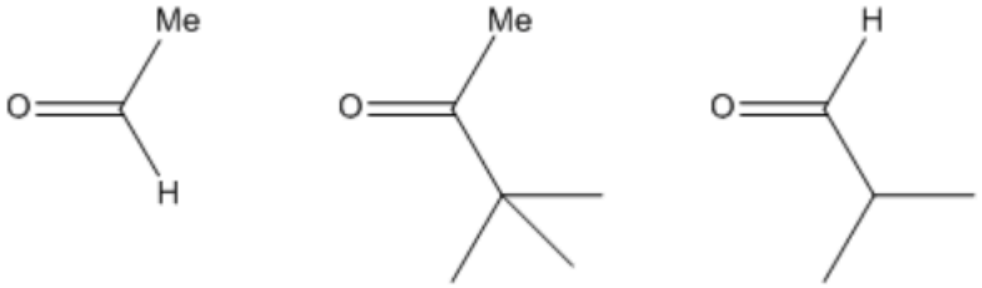
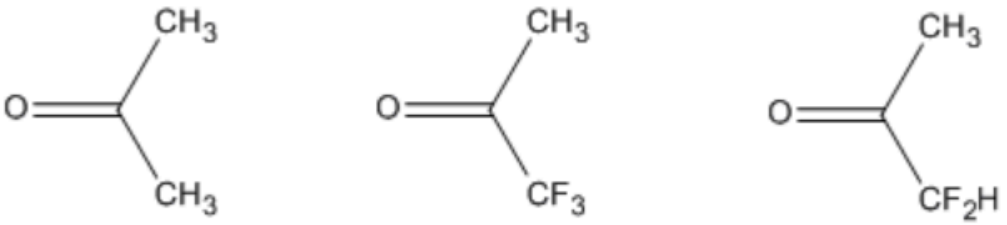
9.1 Nucleophilic Addition to Carbonyl groups: Reactivity

Rank the following compounds in a) and b) from most reactive to least reactive towards nucleophilic addition.

a)

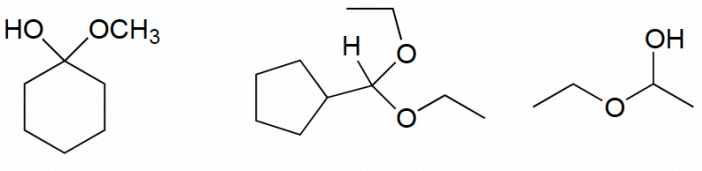


b)

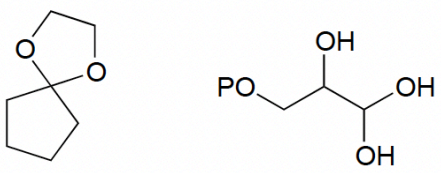


9.2 Acetals and Ketals: Reaction Mechanism

a) Categorize each of the following molecules as a hemiacetal, hemiketal, acetal, ketal, hydrate of an aldehyde, or hydrate of a ketone.



A B C

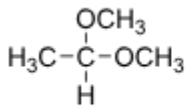


D E

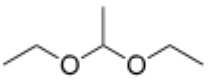
b) Draw the mechanisms for a non-biological acetal formation starting from a hemiacetal catalysed by a strong acid. Does it follow an SN1 or SN2 -type reaction? How does acetal formation in a biochemical context differ from the acid catalyzed acetal formation?

9.3 Acetal/Ketal Formation

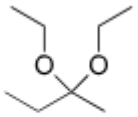
For each acetal/ketal A-D in the figure below, specify the required aldehyde/ketone and alcohol starting materials.



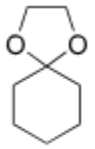
A



B



C

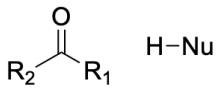


D

9.4 Nucleophilic Additions to Carbonyls: Reaction Mechanism

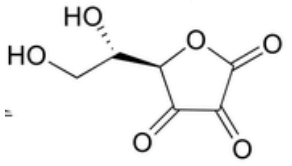
a) Draw the steps of a nucleophilic addition to a carbonyl. Use arrows to indicate the movement of electrons.

b) Assuming that R1 and R2 are non-identical substituents, which enantiomer do you expect for the addition reaction of the following educts?



9.5 Nucleophilic Additions to Carbonyls

You probably know that ascorbic acid (vitamin C) acts as an antioxidant in the body. When vitamin C does its job, it ends up being oxidized to dehydroascobate, which is usually drawn as shown below, in the so-called tricarbonyl form.

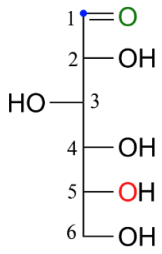


dehydroascorbate
(tricarbonyl form)

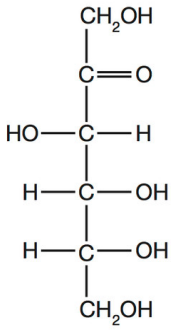
Evidence suggests, however, that the most important form of dehydroascorbate in a physiological context is one in which one of the ketone groups is in its hydrated form, and the other is an intramolecular hemiketal (see Chemical and Engineering News, Aug. 25, 2008, p. 36). Show the structure of this form of dehydroascorbic acid.

9.6 Aldoses and Ketoses: hemiacetals and hemiketals of sugars

a) Sugars can form intramolecular hemiacetals or hemiketals. Draw the resulting 6-ring structure after an intramolecular nucleophilic attack in glucose. What are anomers and how do they form? Reason which anomer is more prevalent in solution? Glucose is shown in its Fischer-Projection below. The numbers 1-6 indicate the carbons. The alcohol highlighted will attack the aldehyde. Hint: glucose in its circular structure will adopt a chair conformation in 3D space.

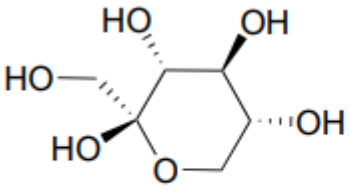


b) In solution, fructose is present in a 5-ring and 6-ring structure. Draw the cyclic structures of fructose. Which ring structure is more common in solution? Why?

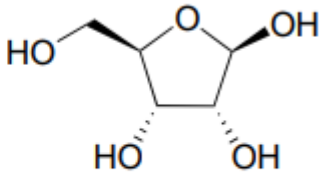


9.7 Sugar chemistry

a. Identify the anomeric carbon of each of the sugars shown below.



sorbose



ribose

b. Draw mechanisms for cyclization of the open-chain forms to the cyclic forms shown above.

9.8 Nucleophilic Addition of Water

Draw for the nucleophilic addition of water to acetone and to formaldehyde the corresponding equilibrium reactions. Which reaction yields more of the hydrate form at equilibrium and why?