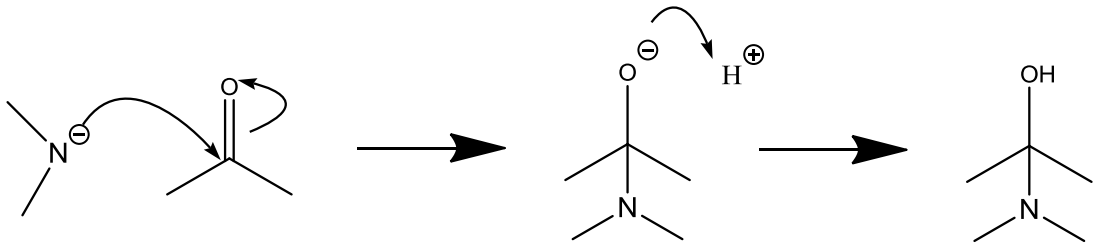
CHEM1611 Worksheet 8: Reactions of Carbonyls

Model 1: Addition to a Carbonyl

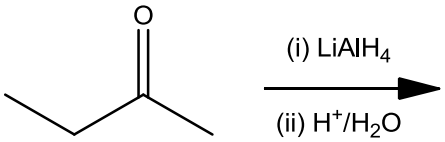
In Worksheet 7, you looked at the following reaction:

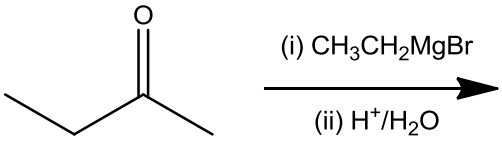


The addition of a nucleophile to a carbonyl carbon is a very general reaction. The C=O bond is very polar and the C end is readily attacked by a nucleophile.

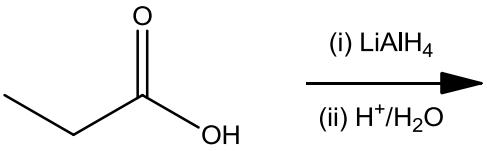
Critical thinking questions

1. Using the model above, predict the outcome of the following reactions. (*Hint*: $LiAlH_4$ reacts as if it contains the hydride ion, H^-, and CH_3CH_2MgBr reacts as if it contains the carbanion, $CH_3CH_2^-$)



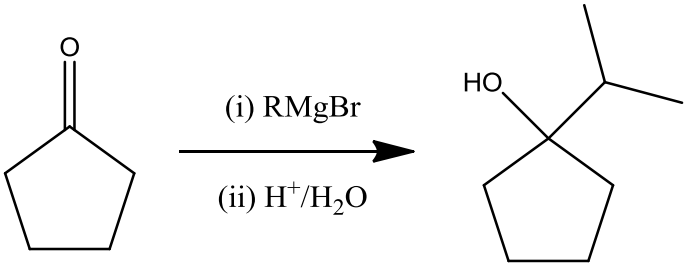


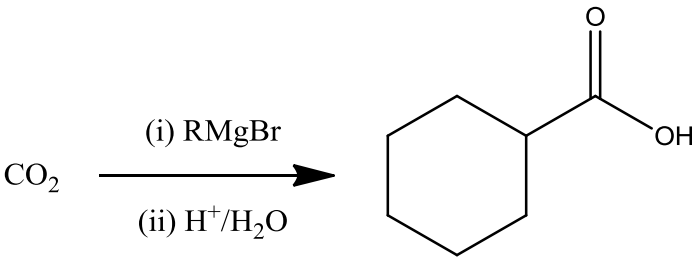
2. Based on this, predict the outcome of the reaction below.



As you saw in worksheet 7, Grignard reagents (RMgBr) are excellent nucleophiles, and are a very good way to form new carbon-carbon bonds.

3. Identify the appropriate Grignard reagent to complete the following reactions.

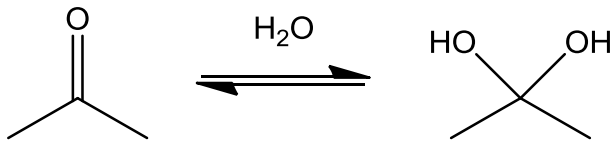




Extension: In each case, the addition of the nucleophile was followed by addition of acid. What purpose does this serve? Why are they not added at the *same* time?

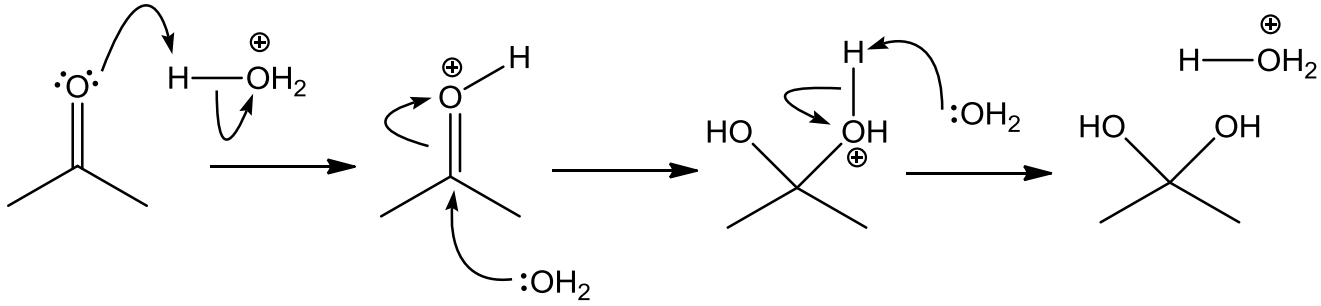
Model 2: Alcohol Addition – Water Elimination

In water, aldehydes and ketones are in equilibrium with hydrates:



ketone hydrate

The mechanism for the acid catalysed formation of hydrates is shown below.

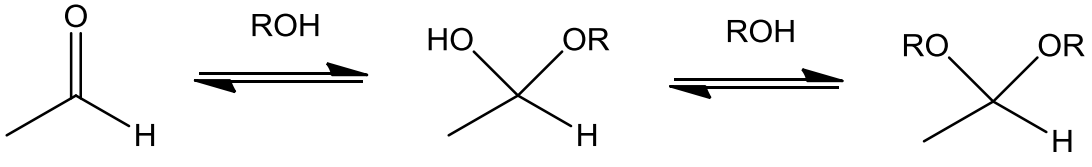


Critical thinking questions

1. Why does acid catalyse the reaction?

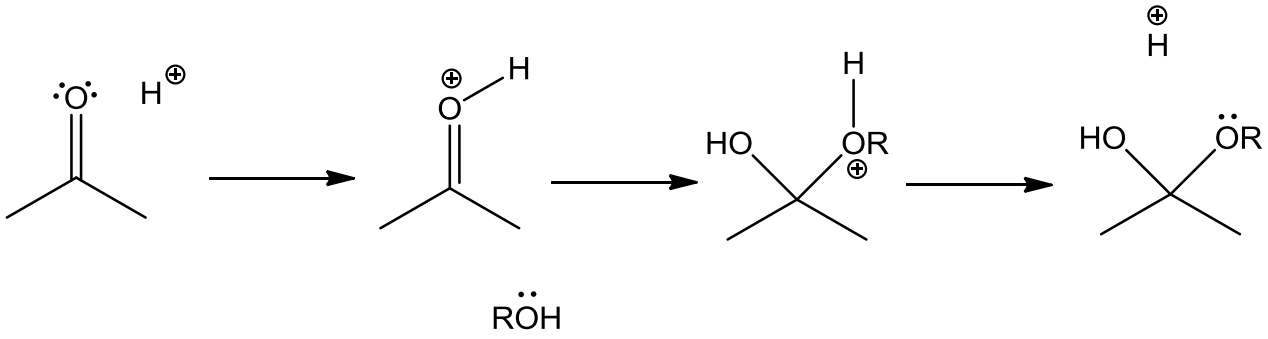
2. In the scheme above, two H_2O molecules react. Describe the two ways in which H_2O is reacting.

Aldehydes and ketones can react in a similar way with alcohols to form hemiacetals and acetals, as shown below.

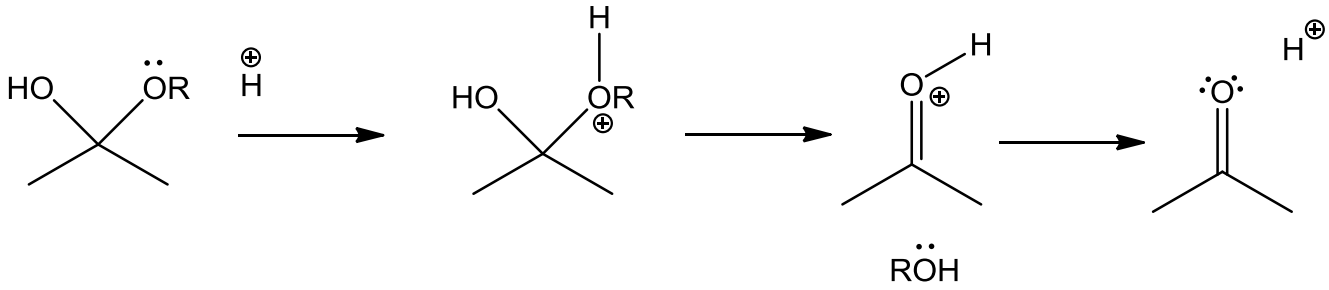


aldehyde hemiacetal acetal

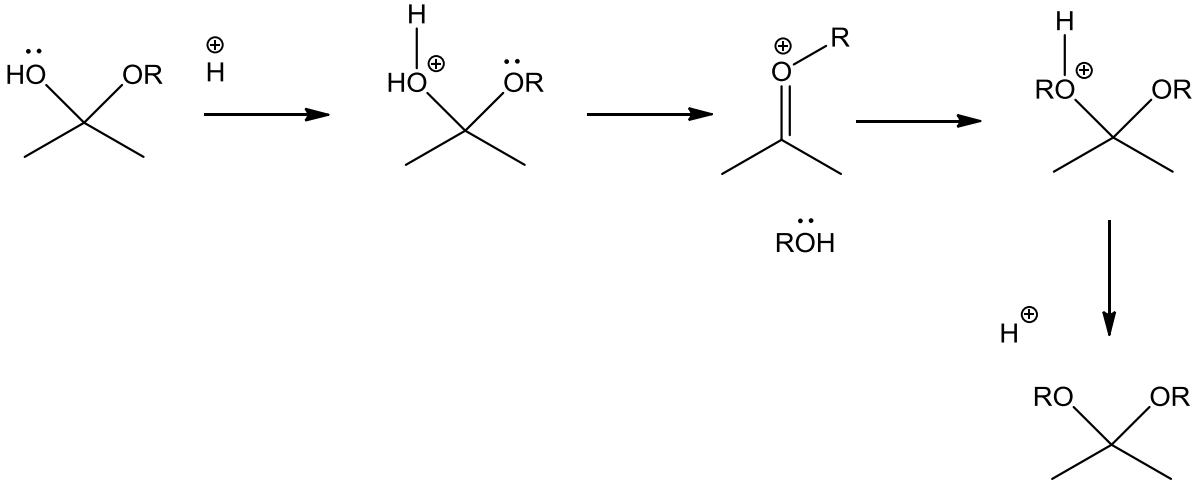
3. Hemiacetal formation follows the same mechanism as hydrate formation, except that an alcohol is the nucleophile instead of water. Add curly arrows to the reaction below to show this.



4. Both hydrate formation and hemiacetal formation are *reversible*. The steps of the reaction are themselves *reversed*. Add curly arrows to the reaction below to show this.

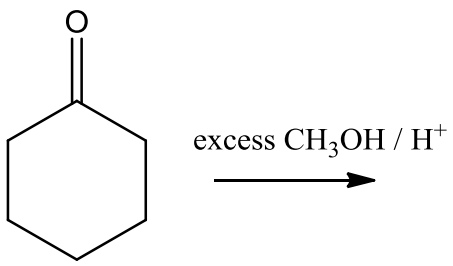


5. Acetal formation from a hemiacetal follows a similar mechanism to the first part of this, as shown below. Add curly arrows to the reaction below to show acetal formation.

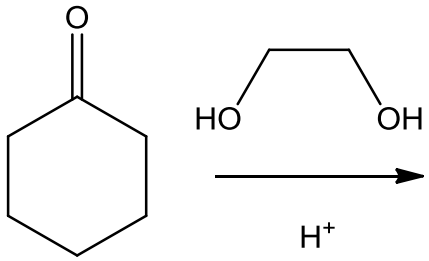


6. Draw the structure of the product(s) formed in the following reactions.

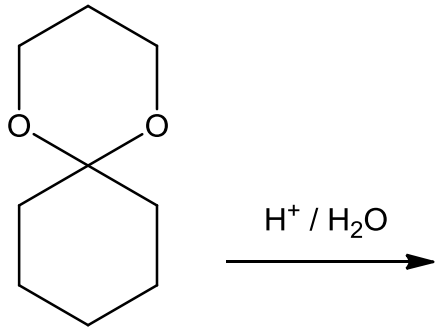
(a)



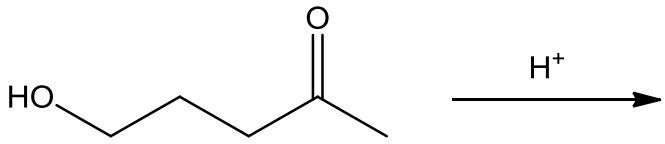
(b)



(c)

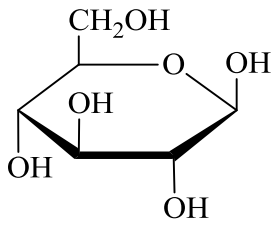


(d)



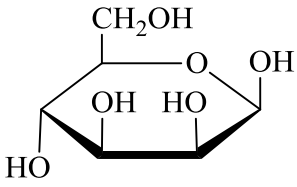
7. Hemiacetals are very important in sugar biochemistry. Circle the hemiacetal in the sugars below and draw the corresponding aldehyde. Do not worry about the stereochemistry. (*Hint*: number the carbon atoms)

(a)



β-D-glucopyranose

(b)



β-D-mannopyranose