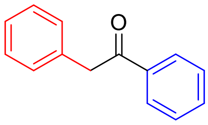
Solutions to Problems - Set 3 : Carbonyl compounds (part 1)

Problem 1

Give the IUPAC name of the following compounds

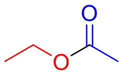
Solution

Ketones:



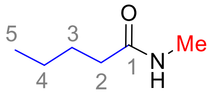
benzyl phenyl ketone
IUPAC: 1,2-diphenylethanone

Esters:



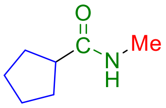
IUPAC: ethyl acetate

Amides:



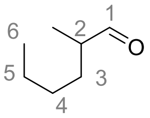
IUPAC: N-methylpentanamide

no "yl" !

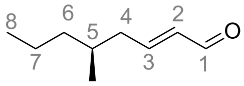


IUPAC: N-methylcyclopentanecarboxamide

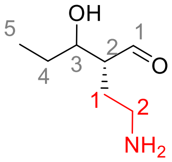
Aldehydes:



IUPAC: 2-methylhexanal



IUPAC: (*S*,*E*)-5-methyloct-2-enal

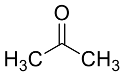


IUPAC:
(2*R*)-2-(2-aminoethyl)-3-hydroxypentanal

Problem 2

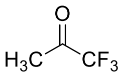
Arrange the following pair of compound in order of expected reactivity toward addition of common nucleophilic agent such as hydroxide ion to the carbonyl bond. Indicate you reasoning?

a)



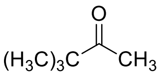
$H_3C-C(=O)-CH_3$

and



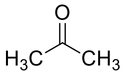
$H_3C-C(=O)-CF_3$

b)



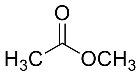
$(H_3C)_3C-C(=O)-CH_3$

and



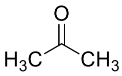
$H_3C-C(=O)-CH_3$

c)



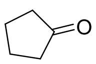
$H_3C-C(=O)-OCH_3$

and

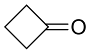


$H_3C-C(=O)-CH_3$

d)



and



Solution

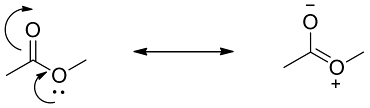
A carbonyl carbon is more susceptible to nucleophilic attack when it is highly electropositive. The nucleophile will more readily contribute its electron pair to a highly electron deficient species in order to relieve the partial positive charge on the carbonyl carbon.

Another important factor determining reactivity is steric hindrance. The bulkier the substituents on the carbonyl group, the less room they have and thus the less active they are.

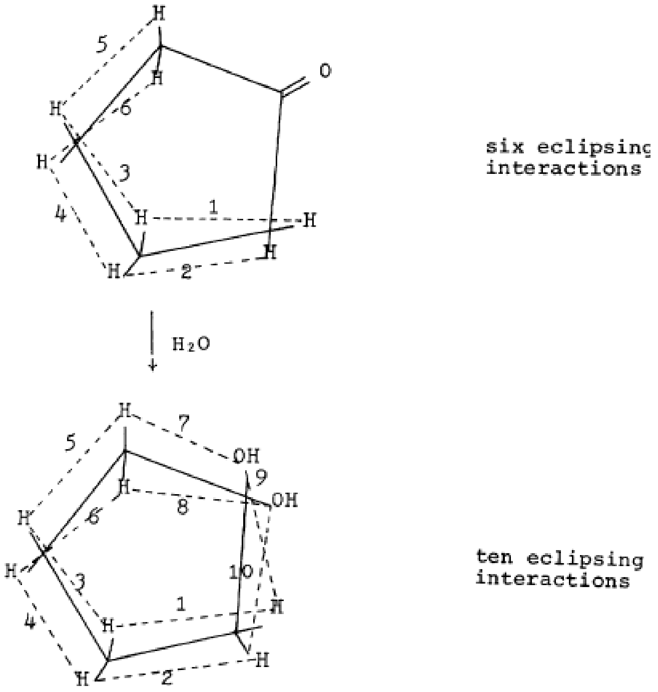
a) The electron withdrawing power of the trichloromethyl group creates a greater **electropositive** charge on carbonyl carbon in CH_3COCF_3. This compound thus is ore reactive to nucleophilic attack.

b) The bulky *t*-butyl group creates great steric hindrance around the carbonyl carbon, thus making the nucleophilic attack very difficult. For this reason, acetone is more active compound.

c) The carbonyl carbon of methyl acetate loses some electropositive charge because of charge stabilization brought about by conjugated resonant structure.



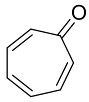
d) For this problem, we should note the carbonyl carbon is sp2 hybridized, and that upon nucleophilic attack it becomes sp3 hybridized. Cyclobutanone has an angle strain of 30^0 (it is the difference between sp2 bond angle 120^0 and cyclobutane bond angle ~ 90^0). Upon nucleophilic addition, the angle strain is reduced to ~20^0 (because the sp3 bond angle is only 109.5^0). So for cyclobutanone there is significant reduction of angle strain. In the case of cyclopentanone, angle strain is not as important as the eclipsing interactions between non-bonded atoms on adjacent carbons.



These eclipsing interactions put more energy in the compound's bonds, thus destabilizing compound. So nuclophilic addition to cyclopentanone is not favorable and cyclobutanone is more active compound.

Problem 3

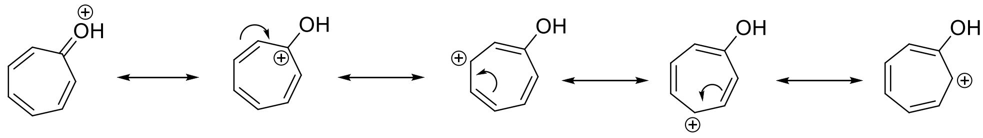
The ketone tropone (below) is exceptionally basic in character, forming much more stable salt with HCl than simple ketone? How can this be explained.



Solution

The ability of a compound to accept for release a proton depends on the stability of the resulting compound. Simple ketones are not basic because protonated compound is too unstable. Since oxygen is very electronegative, it tends to loose positive charge by releasing the proton. Thus, ketone’s basicity is negligible.

The ketone tropone is very different from most other ketones. It displays some aromaticity, although it is not fully aromatic compound.

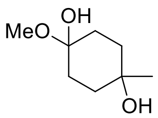


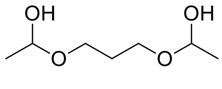
However in protonated form, there are 6 pi electrons in a conjugated flat ring system. It satisfied Hückel’s rule, thus it is aromatic.

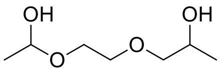
The protonation of tropone creates a positively charged oxygen. This positive charge can be shared by all the ring carbon. The sharing positive charge gives extra stabilization to the resulting compound. Therefore, tropone is more readily protonated or more basic comparing to other ketones.

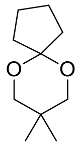
Problem 4

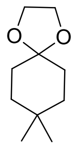
Each compound is a hemi(a)cetal or an (a)cetal. Draw the compounds used to make them and write mechanism for their formation.

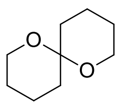








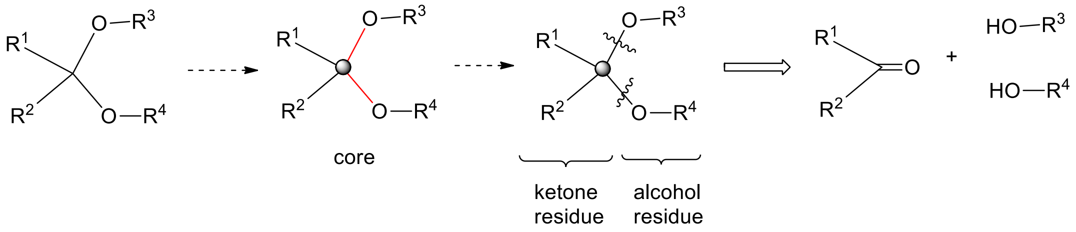




Solution

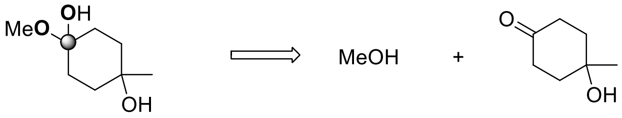
General rule to find precursors of hemi(a)cetal and (a)cetal:

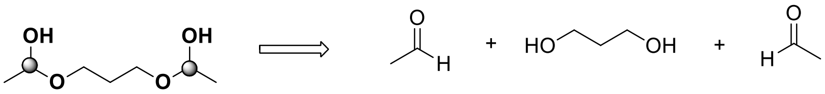
1) Identify the hemiacetal or acetal core (the carbon with 2 C-O bonds)
2) The central carbon atom will become the carbonyl of ketone
3) Break the ether-like C-O bonds to reveal alcohol structures

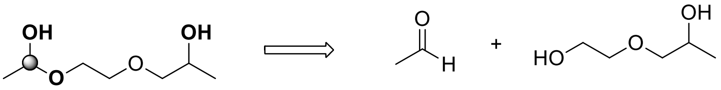


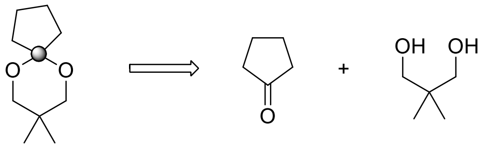
For specific molecules:

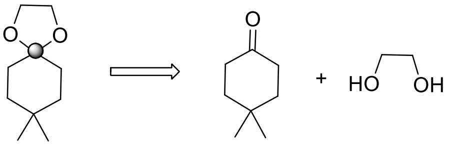
● hemi(a)cetal or (a)cetal core

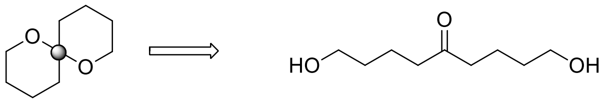






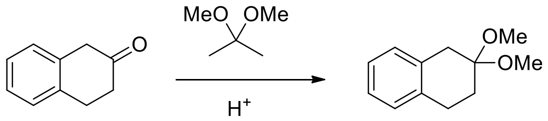


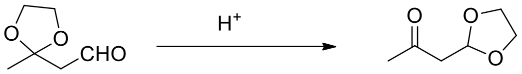




Problem 5

How are the following acetals formed, even though no alcohols are present? For the first reaction, a compound must be distilled from the reaction mixture if it is to go to completion. What is this compound and why it is necessary?

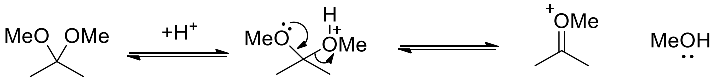




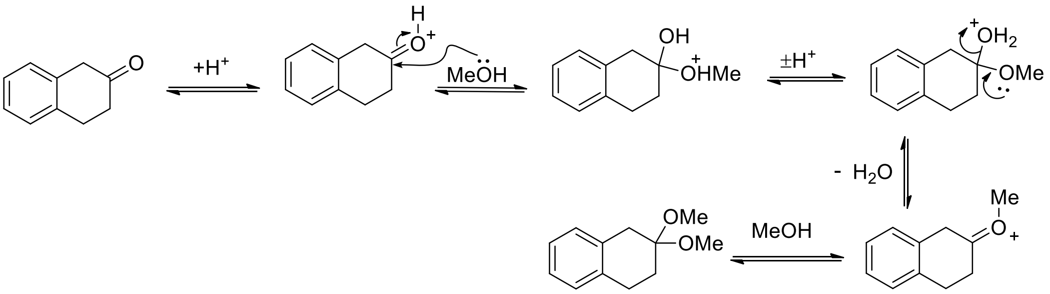
why does the reaction go in this direction?

Solution

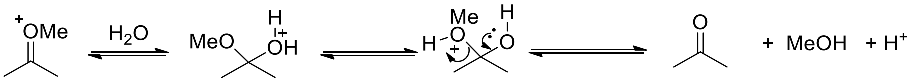
1) In acid, the following equilibrium exists between methyl (a)cetal and methanol



Methanol formed from above can attack other ketone

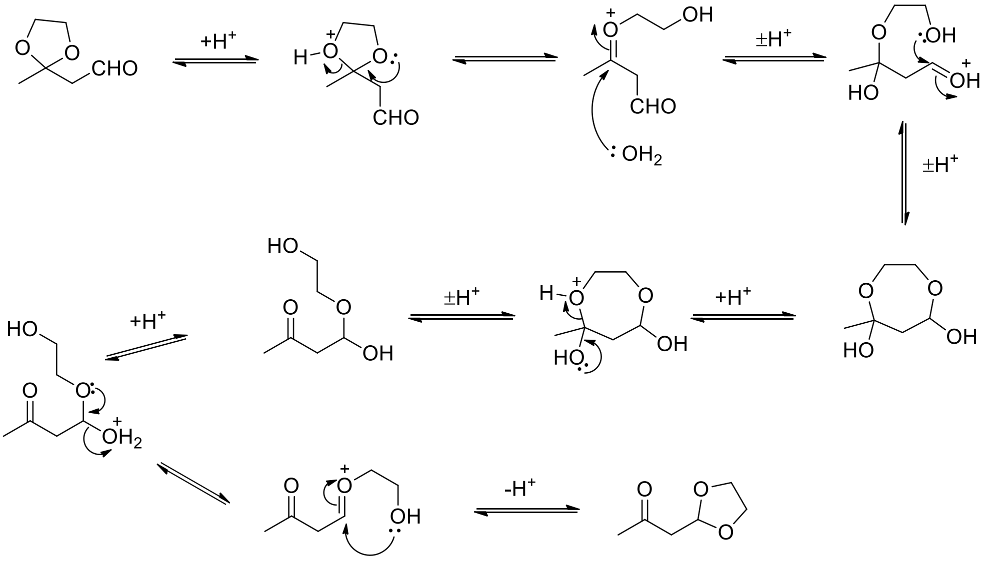


Now, an equivalent of H2O has been generated in this equilibrium. It plays a role in the first mentioned equilibrium:



To induce the reaction to completion, the equilibrium must be destroyed. In this case, acetone may be distilled off from the reaction to pull equilibrium over to products.

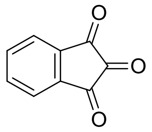
2) In second reaction, acetal center moves from ketone to aldehyde which is less sterically hindered. So the reaction is under thermodynamic control.



Problem 6

a) Cyclopropanone exists as the hydrate in water but 2-hydroxyethanal does not exist as its hemiacetal. Explain?

b) The triketone shown below is called **ninhydrin** and is used for the detection of amino acids. It exists in aqueous solution as a monohydrate. Which carbonyl group of the three ketones is hydrated and why?



ninhydrin

Solution

a) Cyclopropanone is very unstable, it has an angle strain of 60^0 (it is the difference between sp2 bond angle 120^0 and cyclopropanone bond angle ~ 60^0). In the hydrate form, the trigonal carbon is tetrahedral sp3, and the angle strain is reduced to ~49^0 (because the sp3 bond angle is only 109.5^0). The hydrate is more stable than the ketone.

The second case is totally different. Hydroxylethanal is not strained but the hemiacetal has 49^0 of strain at each corner. Even without strain, hydrates and hemiacetal are normally less stable than aldehydes or ketones because one C=O bond is worth more than 2 C-O bonds. In this case the hemiacetal is even less table because of strain.

b) Two ketones next to benzene ring are conjugated with it, and thereby stabilized though they are also destabilized by the middle ketone group. The middle ketone group has no stabilization from the benzene ring and a double dose of destabilization from its neighbors.