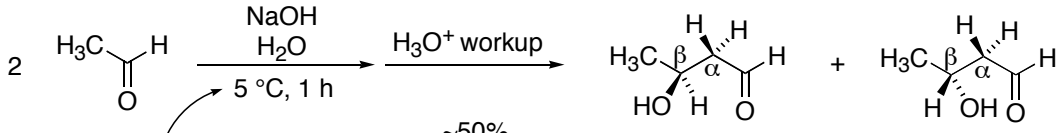
Experiment 6. The Aldol Reaction (or Condensation) [see: Ege's 17.4A, pp 701-705]

The original aldol reaction:

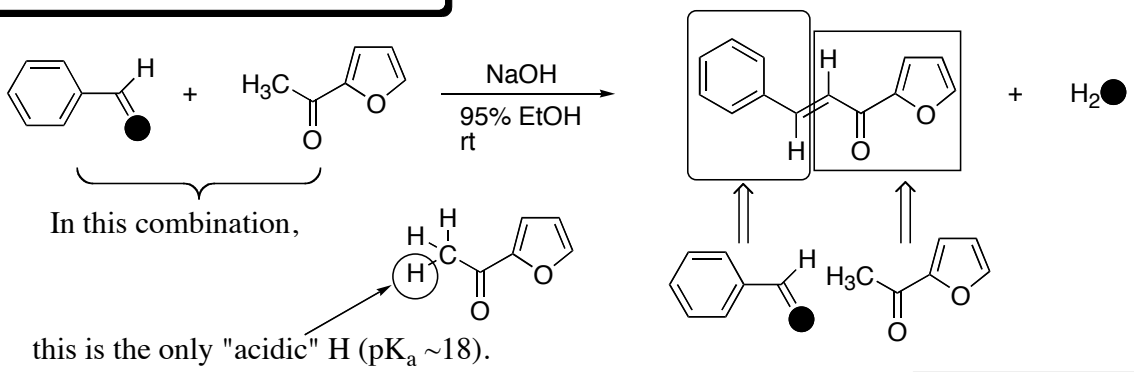


Note these specfic reaction conditions.

Aldol products [**ald**ehyde + **ol**]
(β-hydroxy-aldehyde)

Often difficult to stop at the stage of a β-hydroxy-aldehyde or ketone.

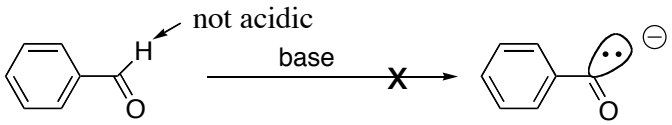
Aldol condensation reaction



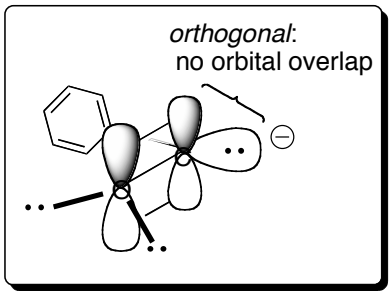
In this combination,

this is the only "acidic" H (pK_a ~18).

Note:

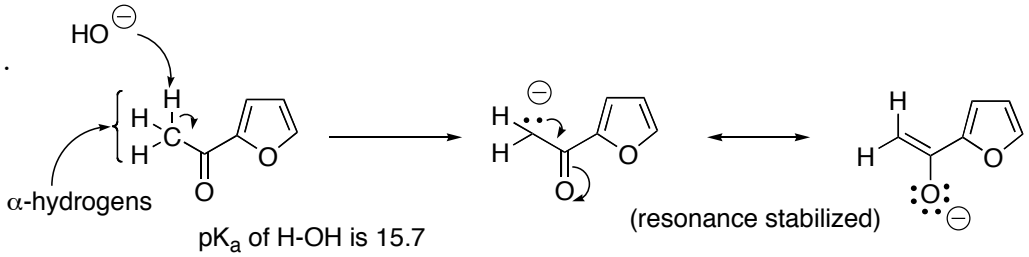


The resulting carbanion is not stabilized by the C=O π-electrons.

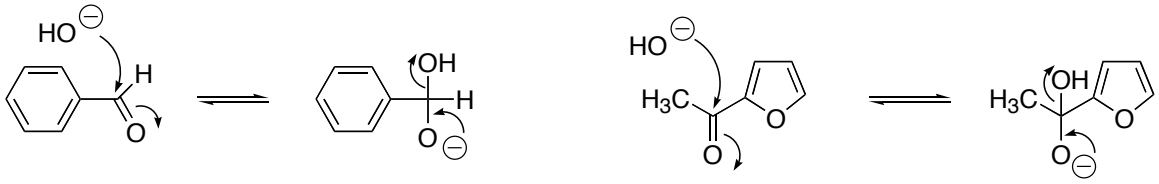


Comments:

1.

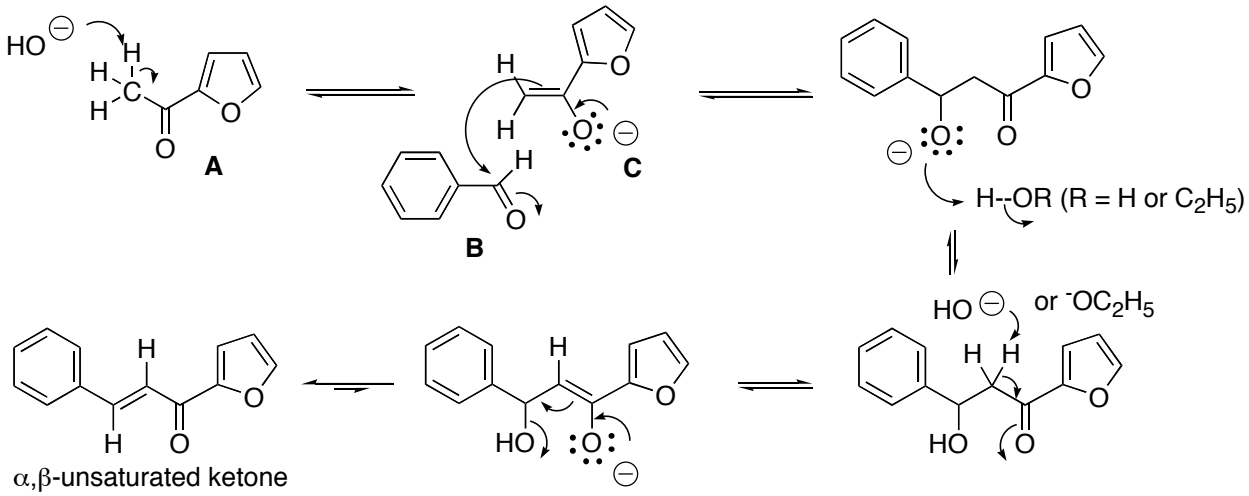


2. Whenever a nucleophilic base (e.g., HO^-, H_3CO^-) is used, the base adds to the C=O carbon.

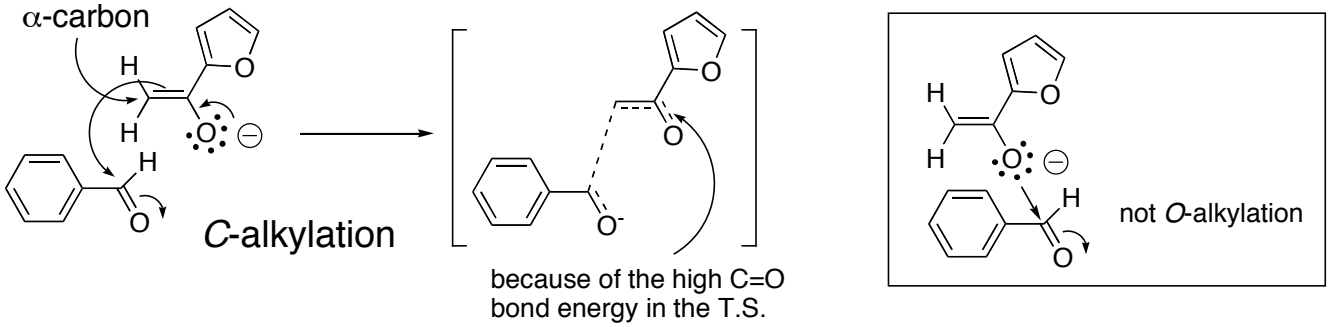


However, these adducted compounds are less stable than the original C=O compounds and do not undergo any other reactions but to go back to the original aldehyde/ketone.

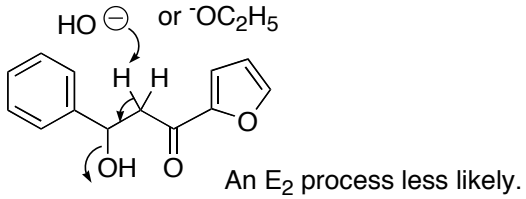
The reaction mechanism:



Comments:
(1) The conjugated ketone produced is primarily the morestable *trans*-stereoisomer.
(2) The reaction of the ketone enolate with benzaldehyde takes place exclusively at the α-carbon.



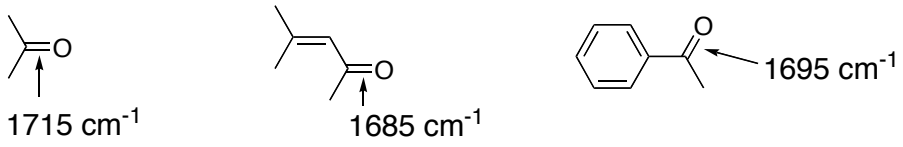
(3) The last dehydration step should go through the ketone enolate intermediate as shown above. The alternative E process should require a higher energy of activation than the pathway that goes through the enolization by deprotonation (acid-base reaction)



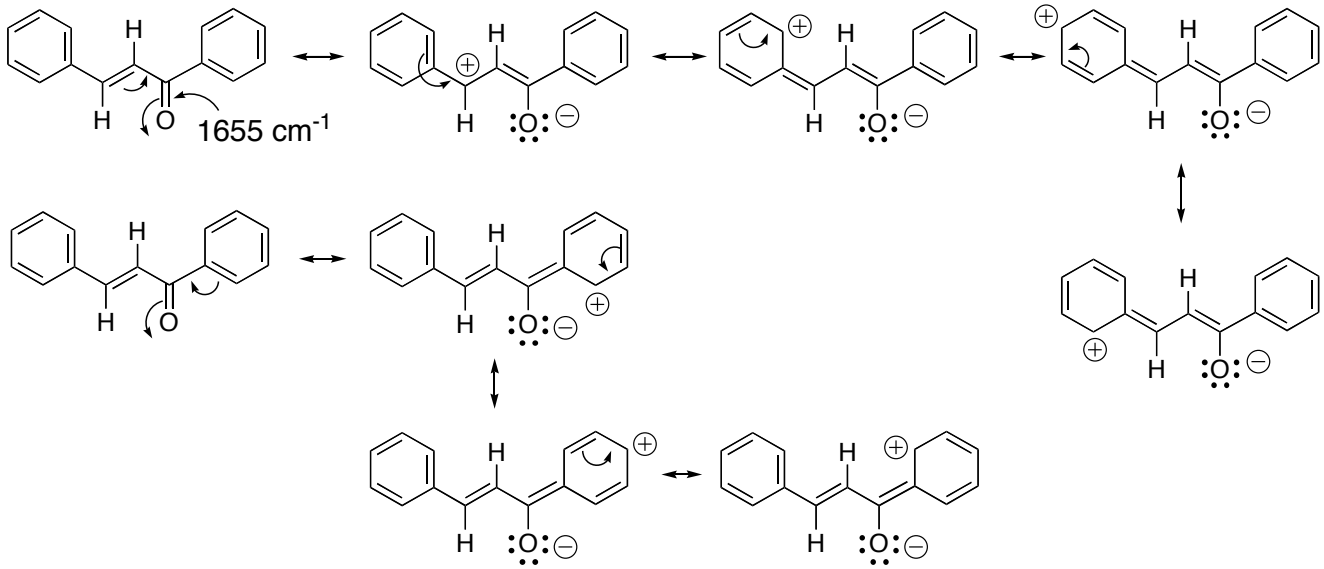
(4) The last dehydration step is thermodynamics driven. Especially, when aromatic ketones/aldehydes are used for the reaction, the resulting α,β-unsaturated ketones are stabilized by extensive resonance involving the alkenic C=C and the two aromatic rings. This is also evident from the extremely low C=O stretching vibration IR absorption bands (~1650 cm^{-1}).

(4) (continued).

νC=O absorption bands:



Aldol condensation product:



All of these resonance structures have the *single-bonded* C-O. ⟶ lowering the νC=O

Questions:

(1) Calculate how many mol equiv of NaOH is used in Experiment 5.

(2) Why does the enolate, **C**, from ketone **A** shown above selectively attack benzaldehyde (**B**) even though a large concentration of non-enolized ketone **A** is available?

(3) Show the structures of the starting carbonyl compounds for the aldol condensation reaction that provides the α,β-unsaturated ketones indicated.