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PLEASE COMPLETE NOTES IN INK AND DO NOT STAPLE.

Aldol rxn

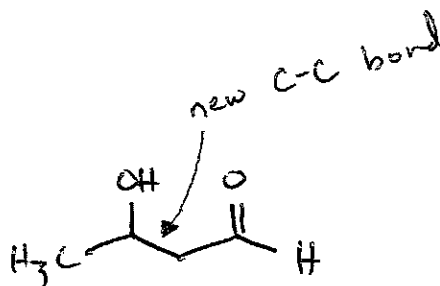
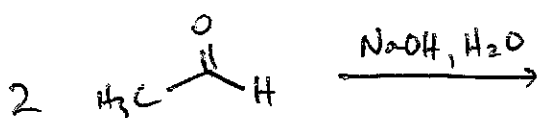
• combines 2 modes of reactivity

1) Nucleophile: α carbon (enol/enolate)

2) Electrophile: carbonyl C

• forms new C-C bonds

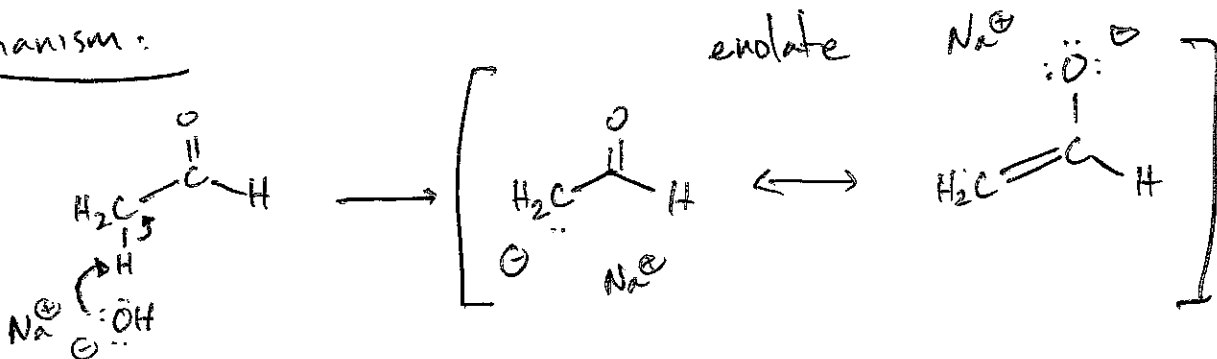
Ex:



β -hydroxy aldehyde

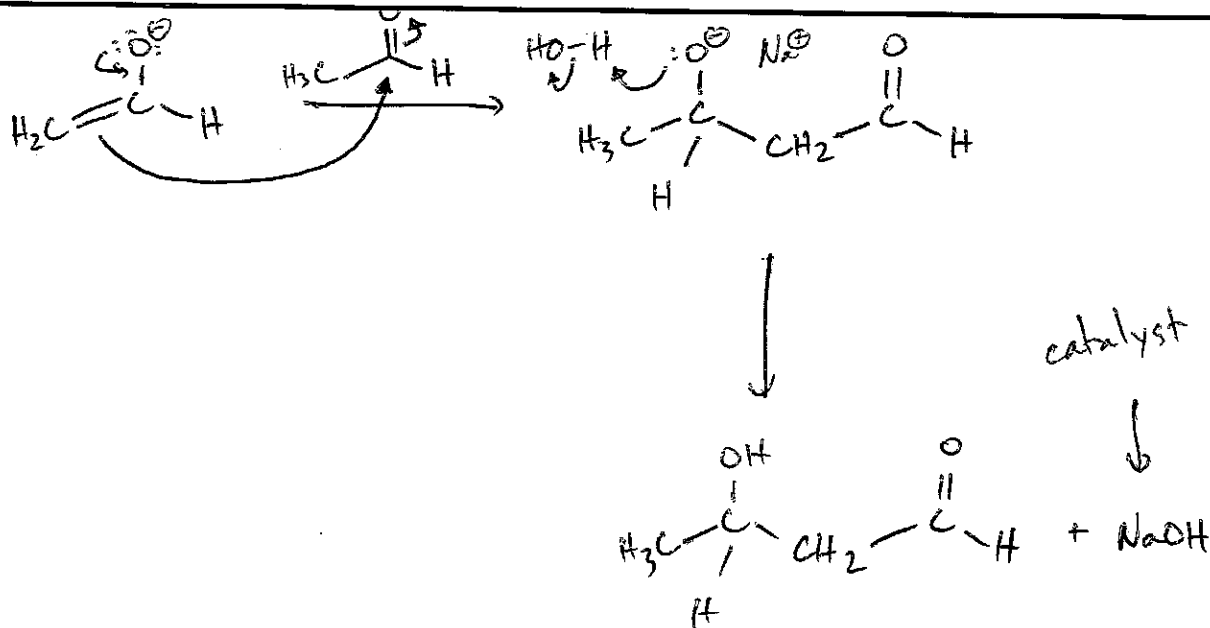
(aldol) aldehyde + alcohol

Mechanism:

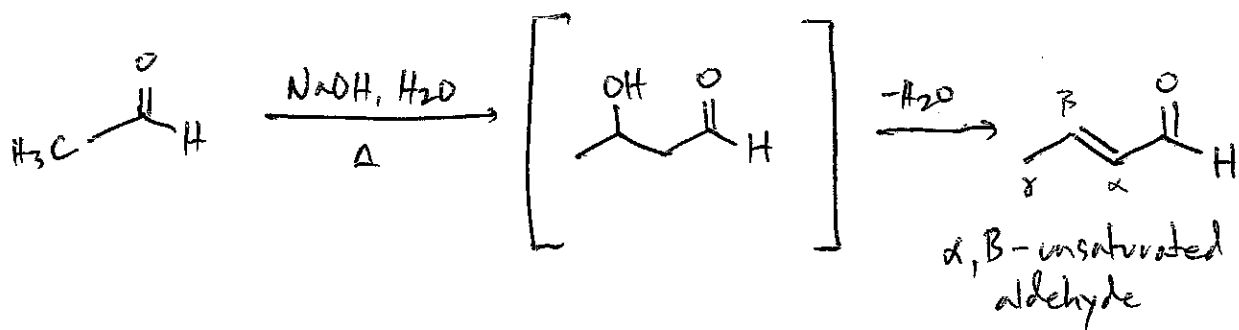


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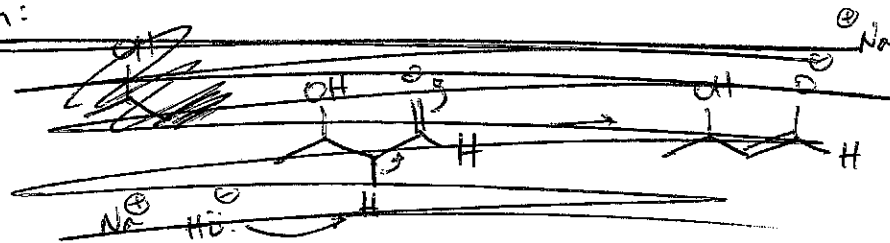
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• Under harsher conditions (e.g. heat), the aldol product can react further by undergoing dehydration.

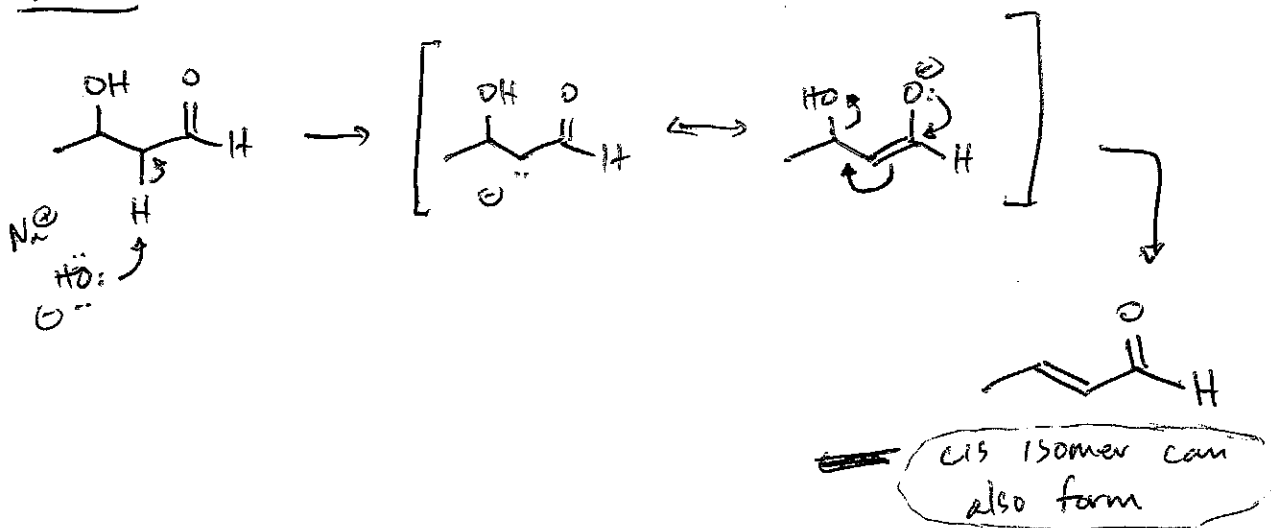


Mech:

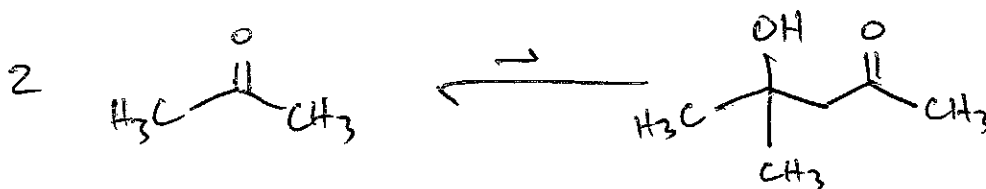
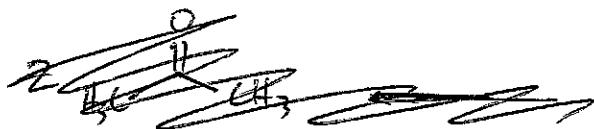


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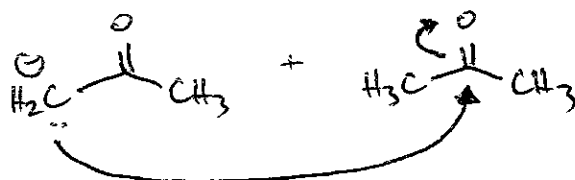
Mech:



- All steps leading to aldol product are reversible.
- Equilibrium favors aldol for aldehydes, but not for ketones



Mech involves:



sterically disfavored relative to aldehydes

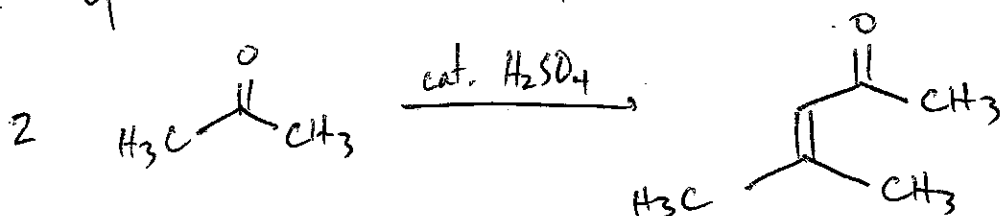
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Aldol: acid-catalyzed

electrophile: protonated aldehyde/ketone

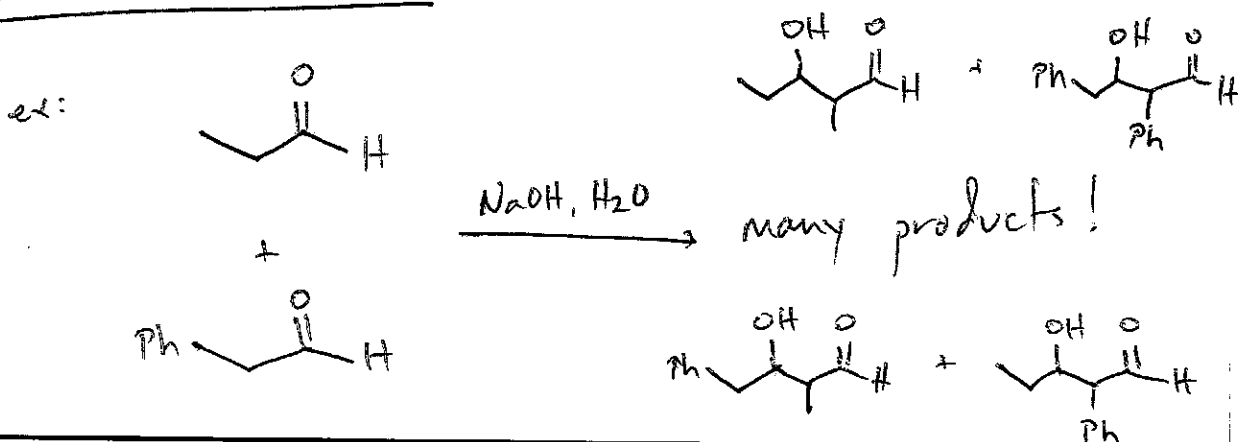
nucleophile: enol

* Look up mechanism for yourself! *



* dehydration is "automatic" under acidic conditions
 * because of dehydration, ketones will proceed to the product (compare to basic version)

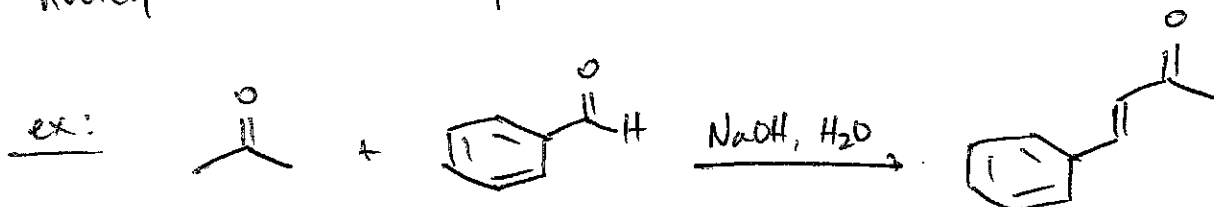
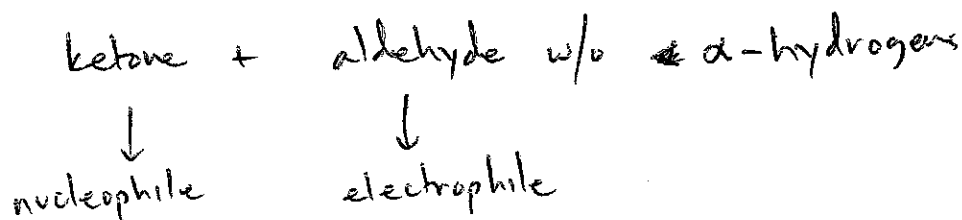
Crossed aldol rxns:



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• you get multiple ppts because the aldehydes can react with themselves (homo-aldol) or with a different aldehyde (crossed-aldol).

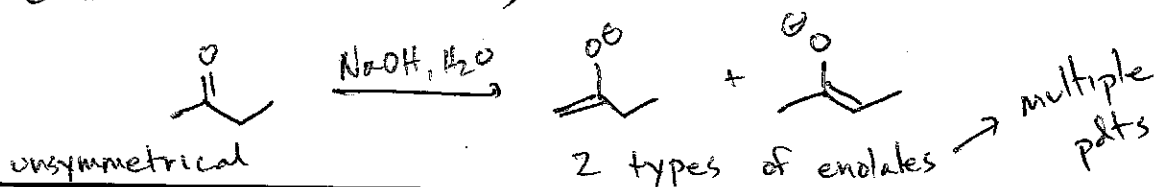
• Special case that provides selectivity:



1) Aldehyde cannot act as the nucleophile
 - no α -hydrogens, can't form enolate

2) Self-condensation rxn of ketone is unfavorable

3) Ketone should be symmetrical (only 1 type of enolate can be formed)

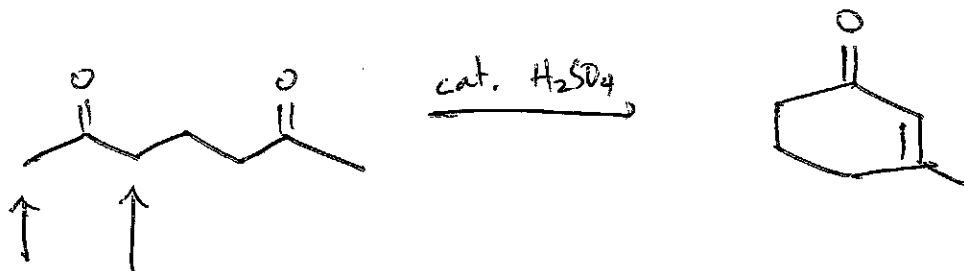


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Intramolecular aldol rxns

- forms 5 or 6-membered ring



~~enol~~ can form at both of the positions, then intramolecular attack can generate a 6- or 4-membered ring.

- 6-membered ring is favored.