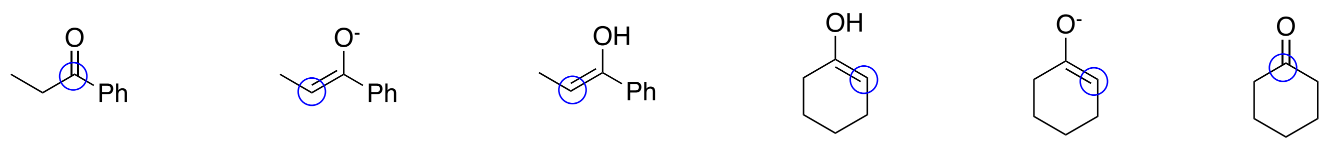
Aldol and Aldol Condensation Reactions

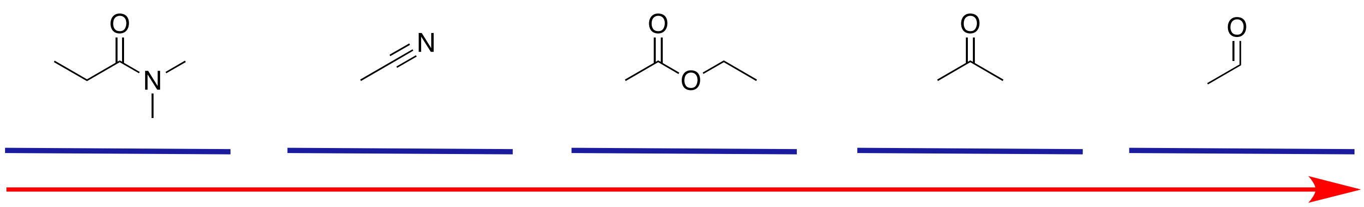
from chapter(s) _______ in the recommended text

A. Introduction

B. Acidities Of Carbonyl Compounds

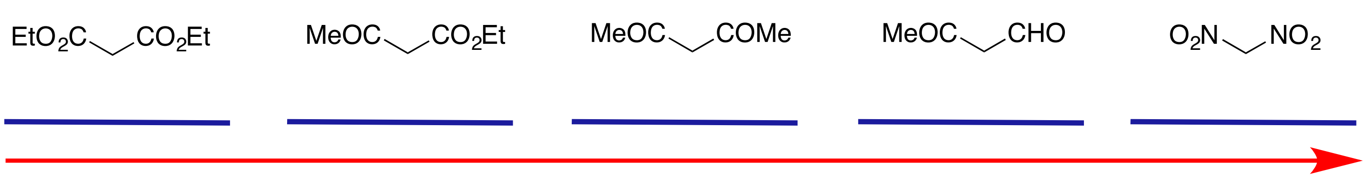


electrophile *nucleophile* *nucleophile* *nucleophile* *nucleophile* *electrophile*



increasingly acidic αCH

less



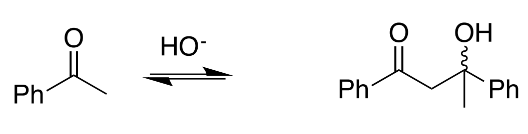
increasingly acidic αCH

more
deprotonated forms.

C. Aldol Reactions

nucleophile

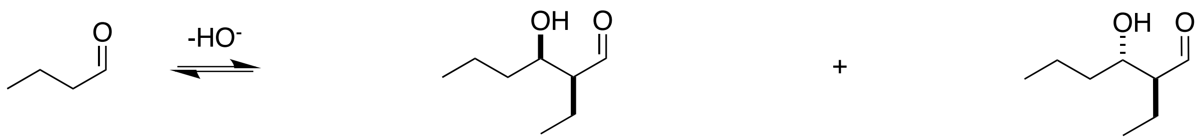
electrophile.



homo-coupling

equal

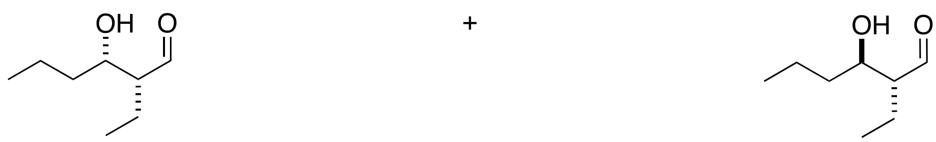
same



syn

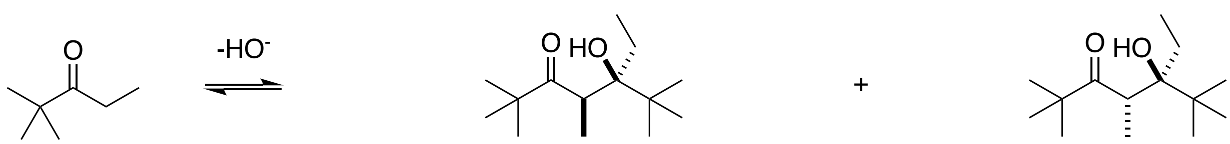
anti

exactly
the same as



syn

anti

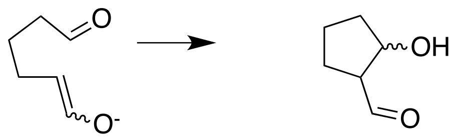


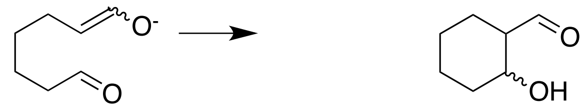
syn

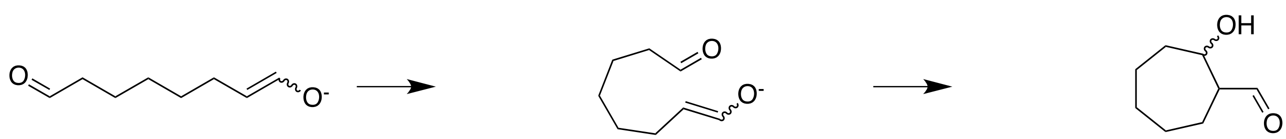
anti

Intramolecular Aldol Reactions

the same molecule.

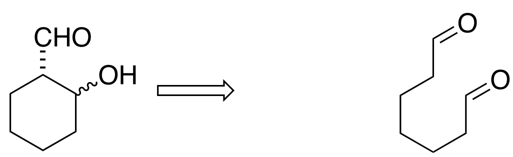


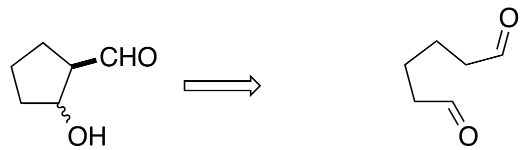


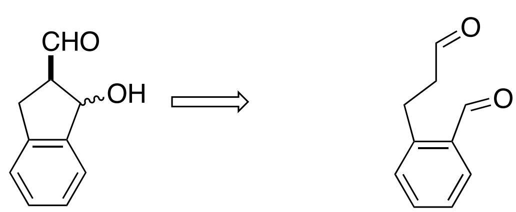


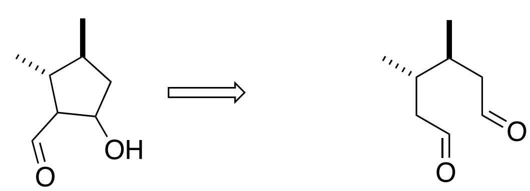
starting material re-drawn

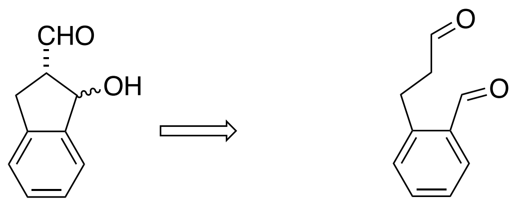
product

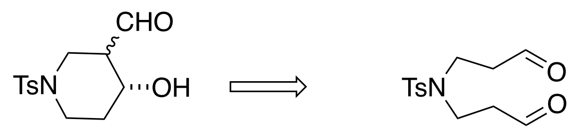




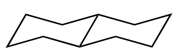




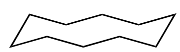




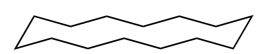
(question changed from 1 st to 2 nd edition)



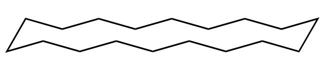
trans-decalin



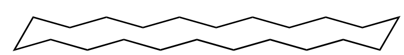
cyclo-$C_{10}H_{20}$



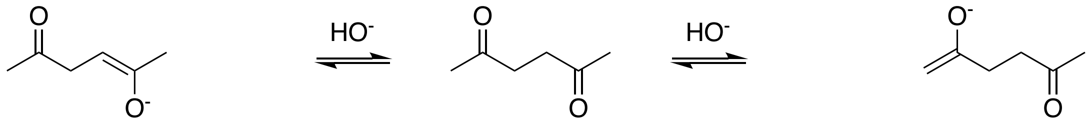
cyclo-$C_{14}H_{28}$



cyclo-$C_{18}H_{36}$

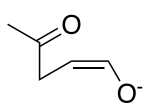


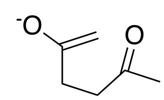
cyclo-$C_{22}H_{44}$



internal enolate
(extended conformation)

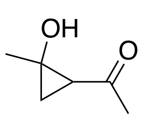
terminal enolate
(extended conformation)

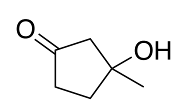




internal enolate
(conformation to give cyclopropane)

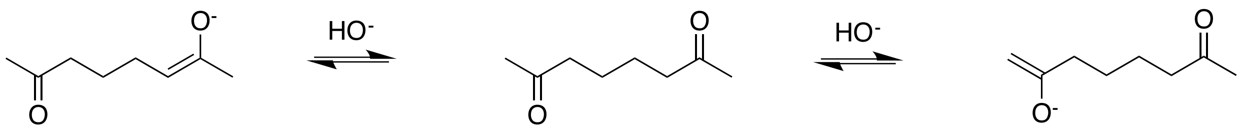
terminal enolate
(conformation to give cyclopentane)





kinetic alkoxide

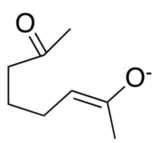
thermodynamic alkoxide



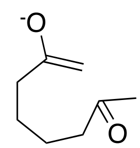
internal enolate
(extended conformation)

2,7-octanedione

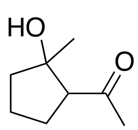
terminal enolate
(extended conformation)



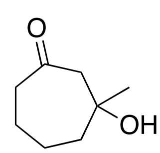
internal enolate
(conformation to give
5-membered ring)



terminal enolate
(conformation to give
7-membered ring)

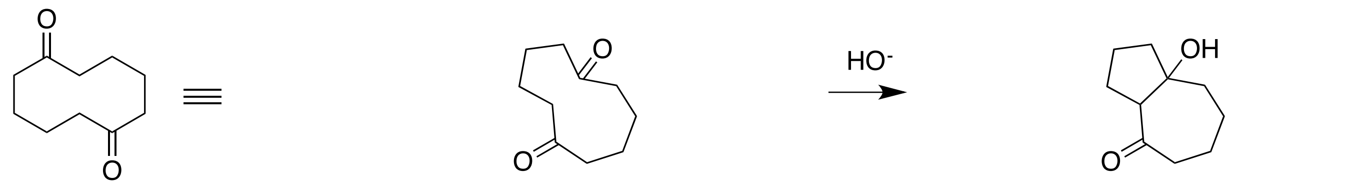


alkoxide from a cyclopentanol



alkoxide from a cycloheptanol

neither the thermodynamic or the kinetic product.

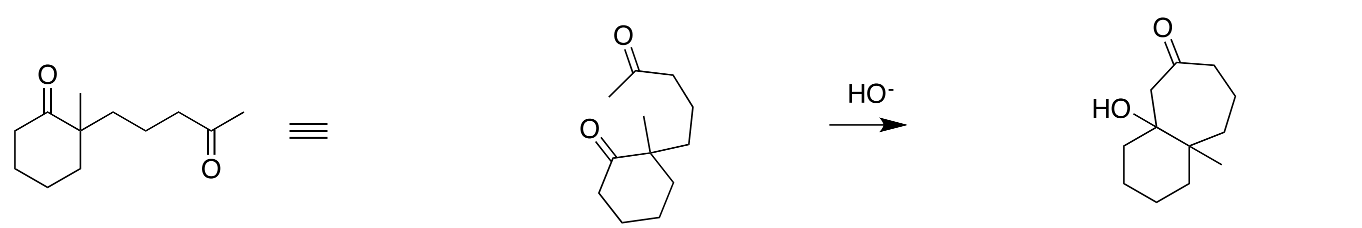


starting material re-drawn

product
(edge shared
7 and 5-membered rings)

starting material re-drawn

product



starting material re-drawn

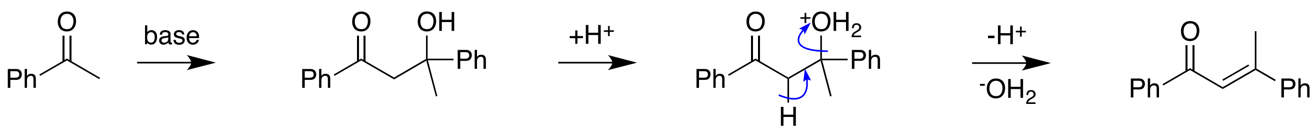
favored product

starting material re-drawn

favored product

D. Dehydration Of Aldol Products: Aldol Condensations

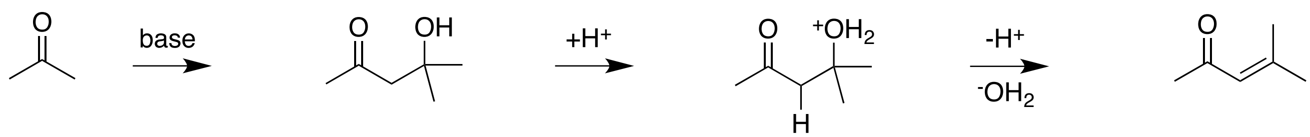
Homocouplings



aldol product after protonation with water

oxonium

enone



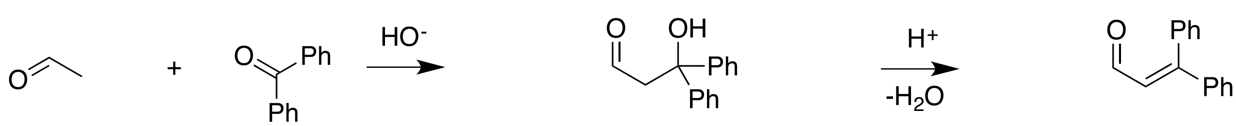
aldol product after protonation with water

oxonium

enone

Cross Condensations

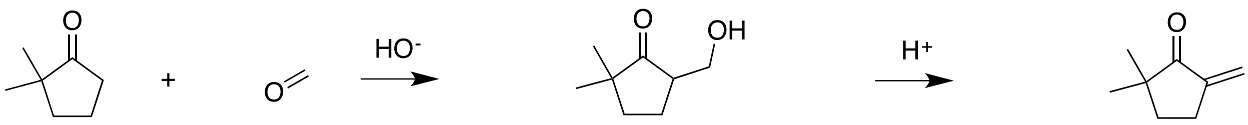
Featuring One Enolizable Component



intermolecular cross aldol

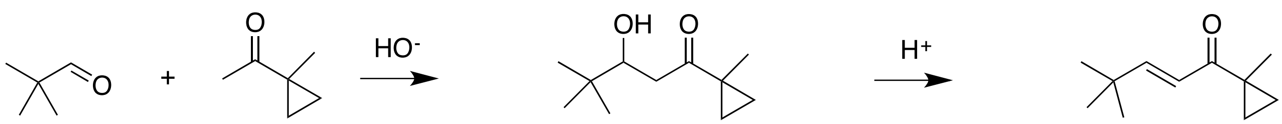
enone

more reactive



intermolecular aldol

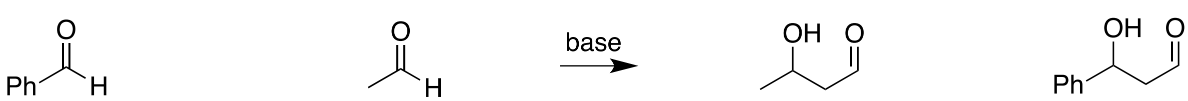
dehydration to enone



intermolecular aldol

dehydration to enone

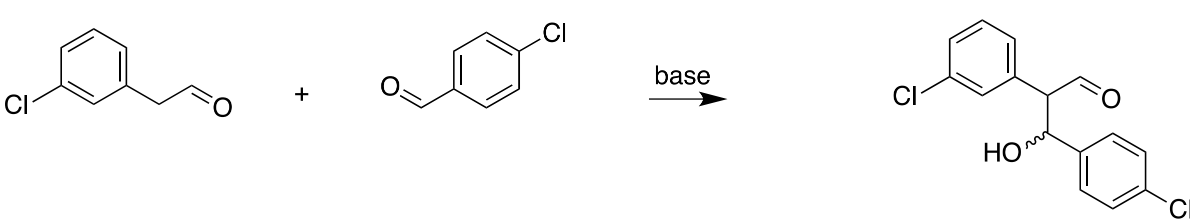
One
one of the components



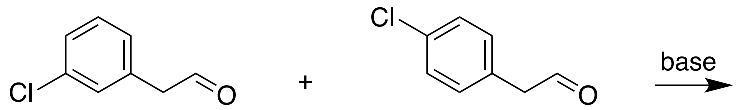
benzaldehyde + *ethanal*

homocoupling product + *heterocoupling product (ie cross coupling)*

benzaldehyde and the one added slowly to this would be *ethanal*.

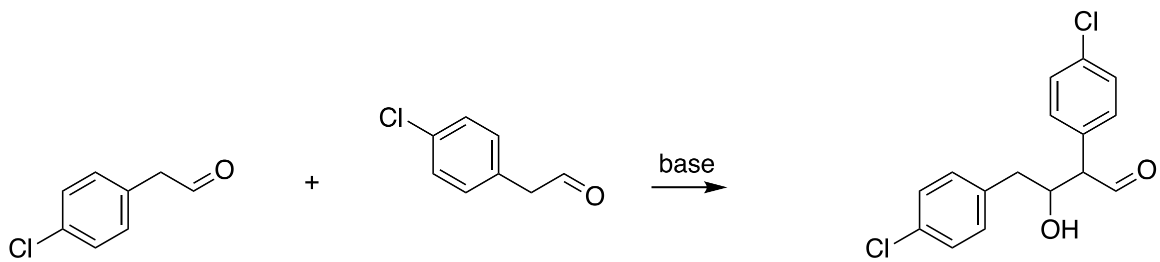


heterocoupling product
(ie cross coupling)

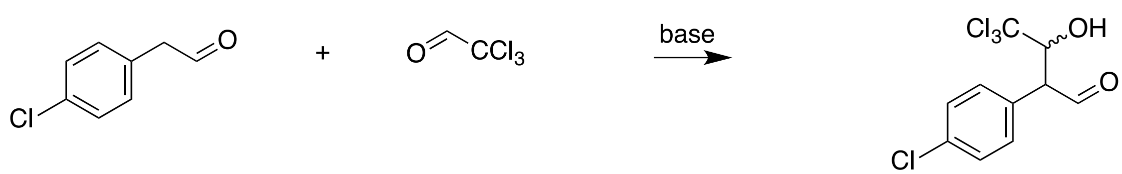


mixture

heterocoupling product
(ie cross coupling)

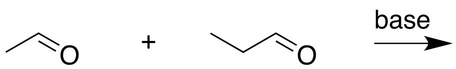


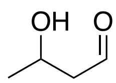
homocoupling product



heterocoupling product
(ie cross coupling)

Aldol Condensations Are Hard To Control When Two Enolizable Fragments Are Used





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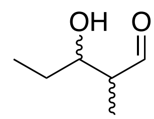

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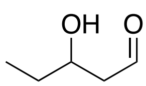
homocoupling product 1

homocoupling product 2
(two diastereomers)



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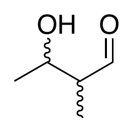
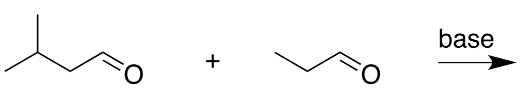
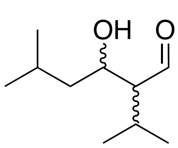


heterocoupling product 1

heterocoupling product 2
(two diastereomers)





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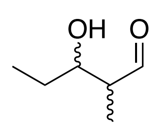

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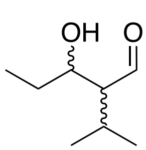
homocoupling product 1

homocoupling product 2
(two diastereomers)



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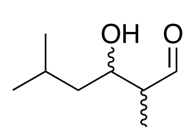

heterocoupling product 1

heterocoupling product 2
(two diastereomers)

Intramolecular Condensations