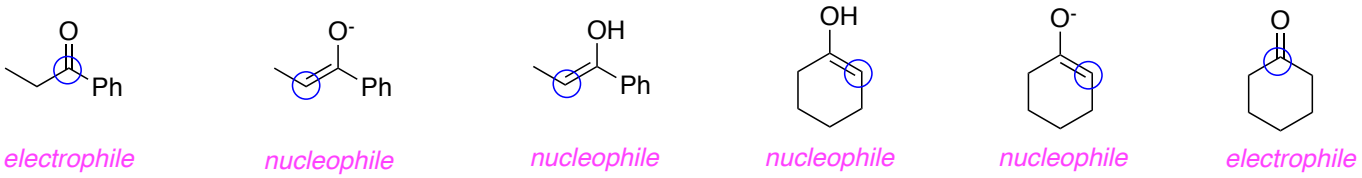
Aldol and Aldol Condensation Reactions

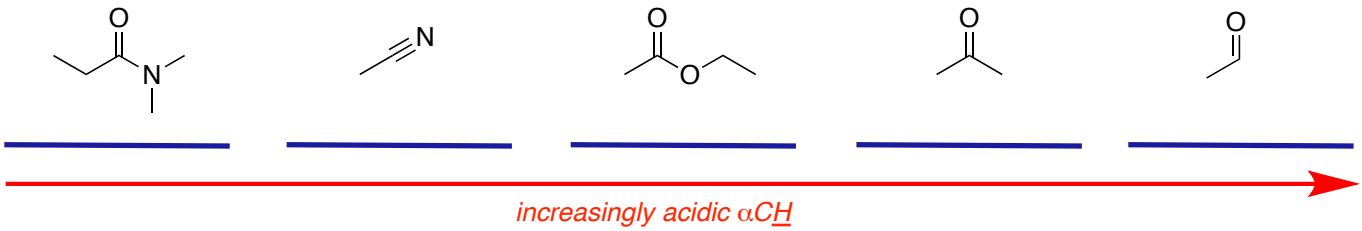
from chapter(s) _____ in the recommended text

A. Introduction

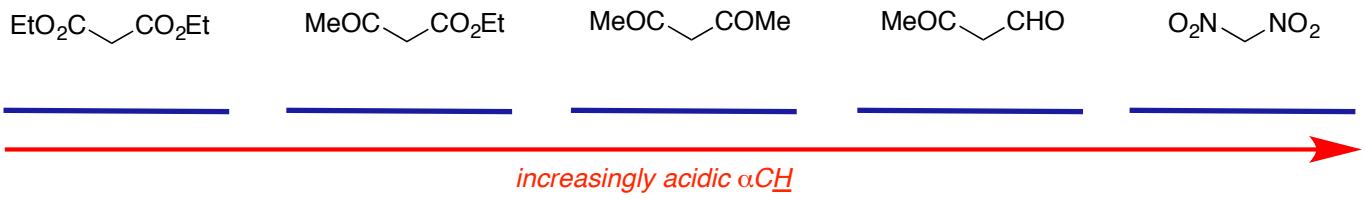
B. Acidities Of Carbonyl Compounds



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



less

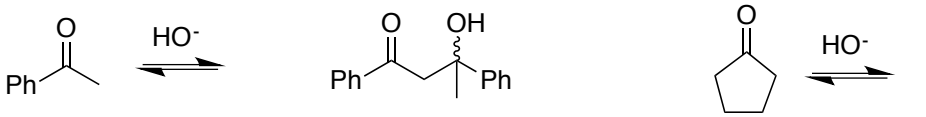


more
deprotonated forms.

C. Aldol Reactions

nucleophile

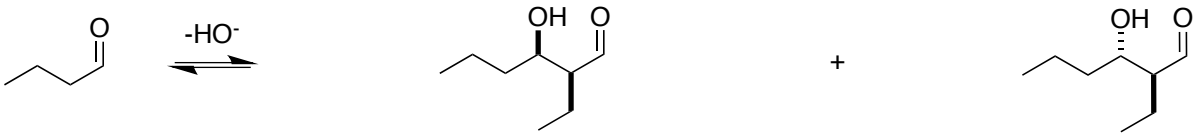
electrophile.



homo-coupling

equal

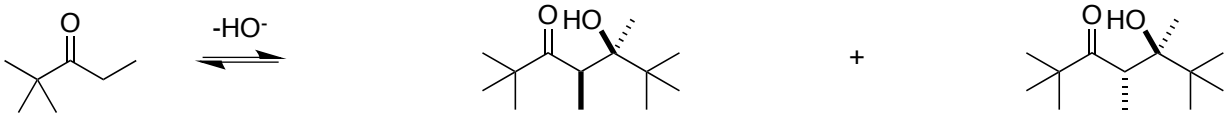
same



syn *anti*

exactly
the same as

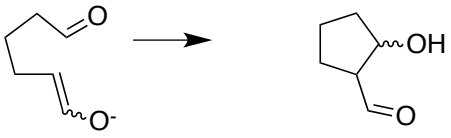
syn *anti*

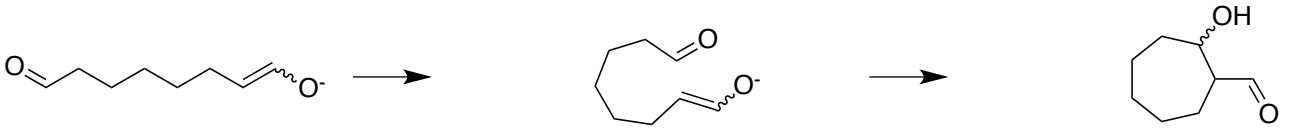


syn *anti*

Intramolecular Aldol Reactions

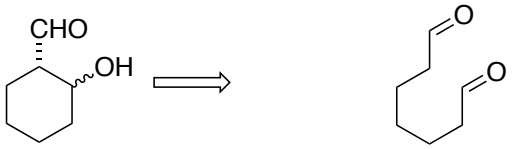
the same molecule.

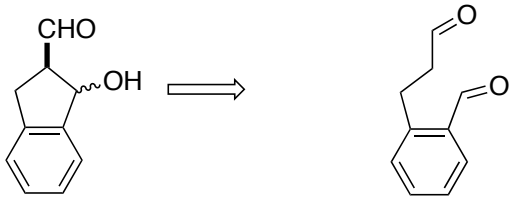


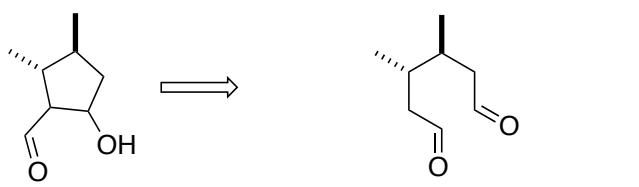


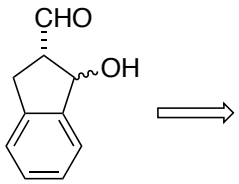
starting material re-drawn

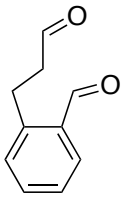
product

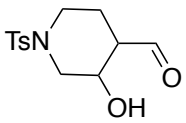


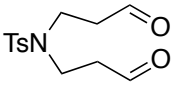


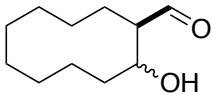


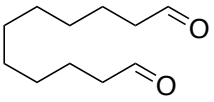




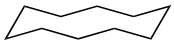




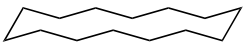




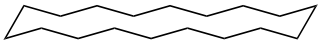
trans-decalin



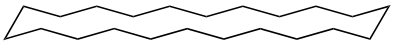
cyclo-$C_{10}H_{20}$



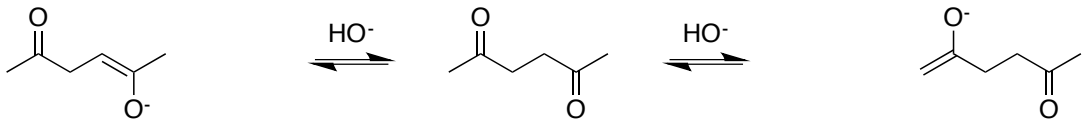
cyclo-$C_{14}H_{28}$



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

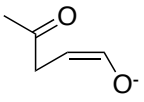


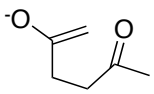
cyclo-$C_{22}H_{44}$



internal enolate
(extended conformation)

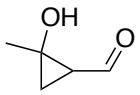
terminal enolate
(extended conformation)

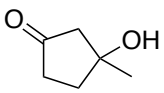




internal enolate
(conformation to give cyclopropane)

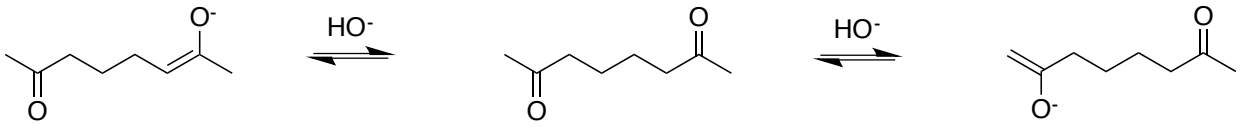
terminal enolate
(conformation to give cyclopentane)





kinetic alkoxide

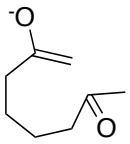
thermodynamic alkoxide



internal enolate
(extended conformation)

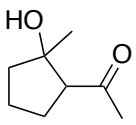
2,7-octanedione

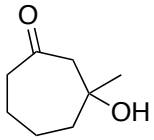
terminal enolate
(extended conformation)



internal enolate
(conformation to give
5-membered ring)

terminal enolate
(conformation to give
7-membered ring)

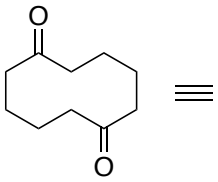




alkoxide from a cyclopentanol

alkoxide from a cycloheptanol

neither the thermodynamic or the kinetic product.



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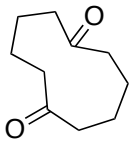
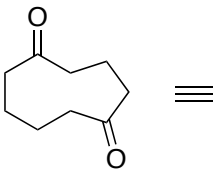


starting material re-drawn

product
(edge shared
7 and 5-membered rings)



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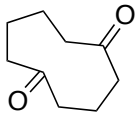
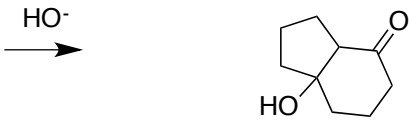
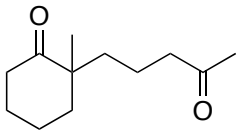




starting material re-drawn

product



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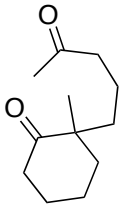
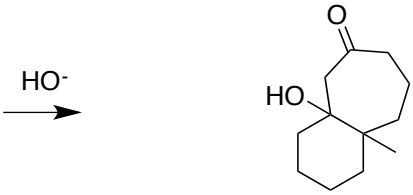
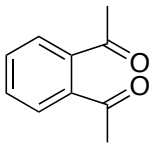




starting material re-drawn

favored product



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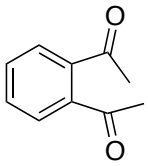
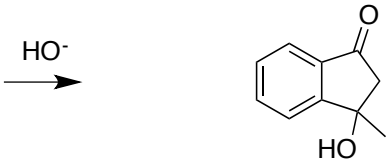


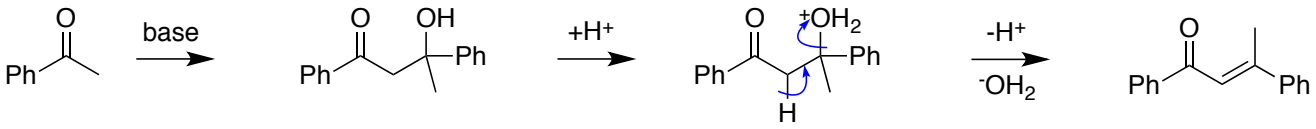


starting material re-drawn

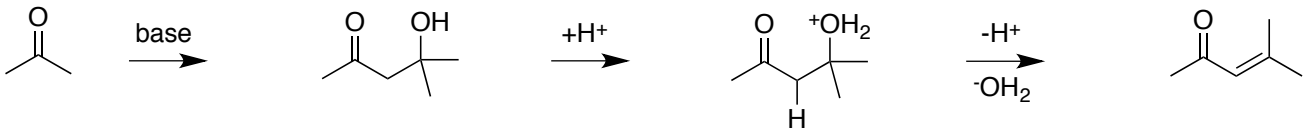
favored product

D. Dehydration Of Aldol Products: Aldol Condensations

Homocouplings



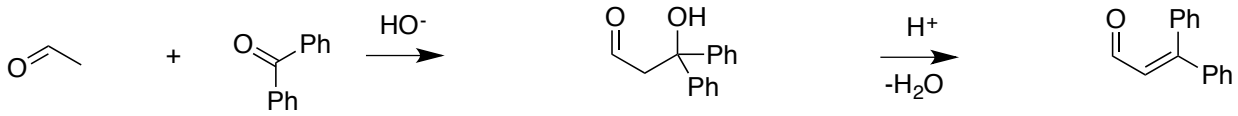
aldol product after protonation with water | *oxonium* | *enone*



aldol product after protonation with water | *oxonium* | *enone*

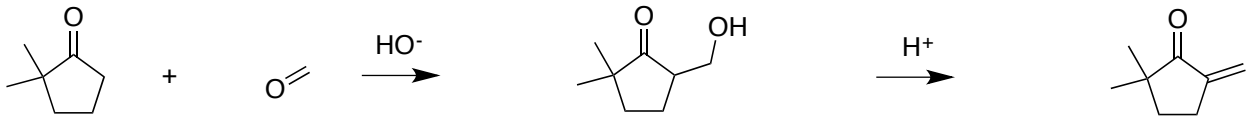
Cross Condensations

Featuring One Enolizable Component

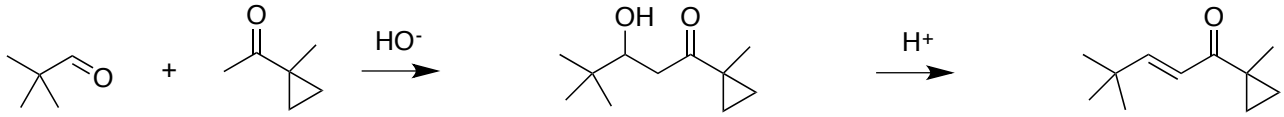


intermolecular cross aldol | *enone*

more reactive

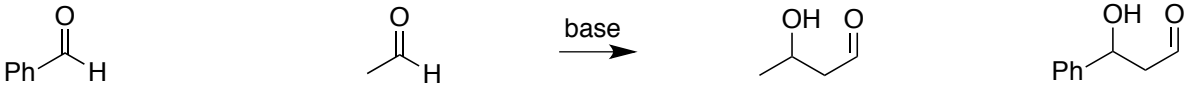


intermolecular aldol *dehydration to enone*



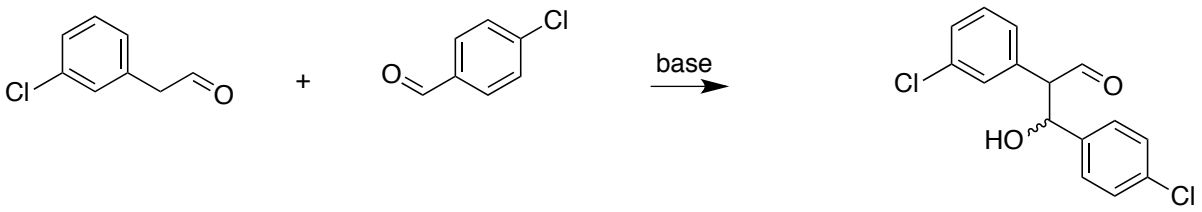
intermolecular aldol *dehydration to enone*

One
one of the components

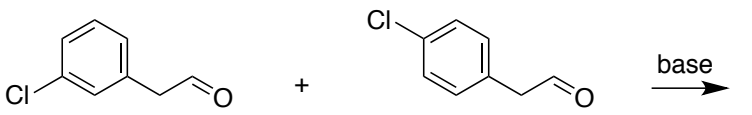


benzaldehyde + *ethanal* *homocoupling product* + *heterocoupling product (ie cross coupling)*

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

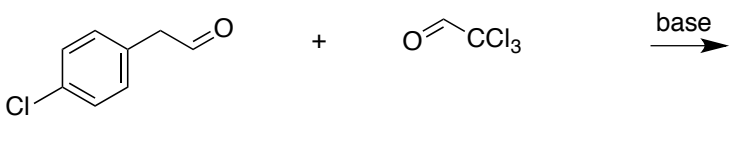


heterocoupling product (ie cross coupling)



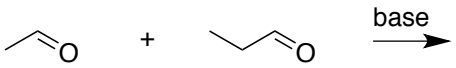
mixture

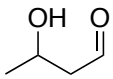
heterocoupling product
(ie cross coupling)



heterocoupling product
(ie cross coupling)

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





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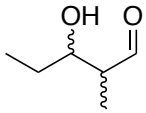

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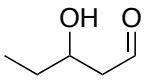
homocoupling product 1

homocoupling product 2
(two diastereomers)



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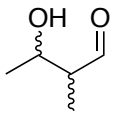
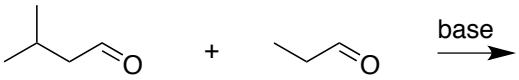
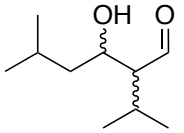


heterocoupling product 1

heterocoupling product 2
(two diastereomers)





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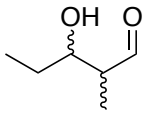

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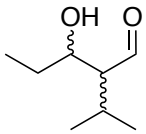
homocoupling product 1

homocoupling product 2
(two diastereomers)



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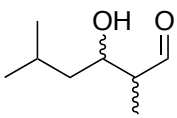

heterocoupling product 1

heterocoupling product 2
(two diastereomers)

Intramolecular Condensations