

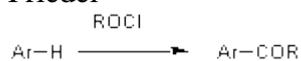
Question #61077 – Chemistry – Organic Chemistry

Question 1. Write main reaction types used for skeleton building.

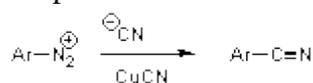
Answer:

In aromatic chemistry:

Friedel Crafts type reactions



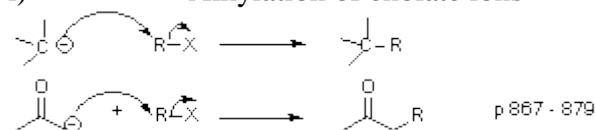
Displacements on aromatic diazonium salts



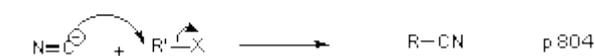
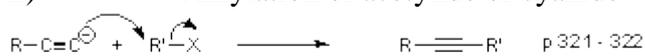
Grignard reagents + carbonyls)

Carbanion Alkylation

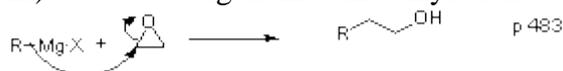
i) Alkylation of enolate ions



ii) Alkylation of acetylide or cyanide

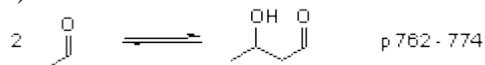


iii) Organometallic alkylation

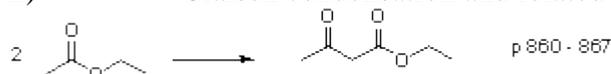


Carbonyl Addition And Carbonyl Substitution Reactions

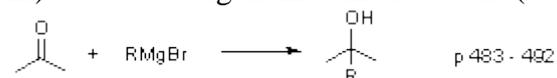
i) Aldol and related reactions (Addⁿ)



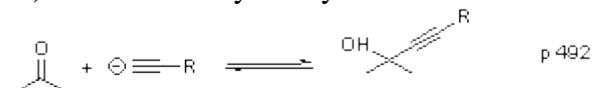
ii) Claisen condensation and related reactions (Subⁿ)



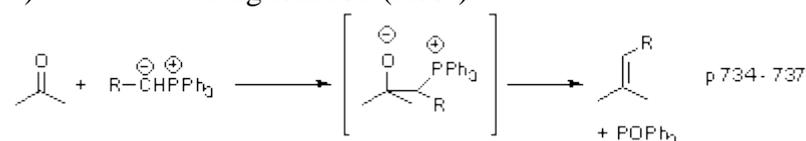
iii) Organometallic reactions (Addⁿ)



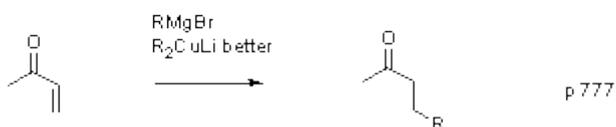
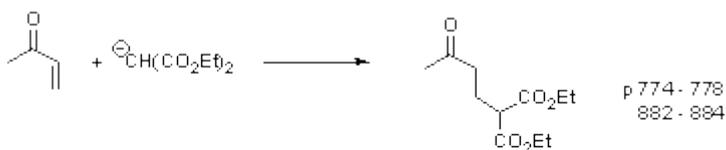
iv) Acetylide/cyanide addition



v) Wittig reaction (Addⁿ)



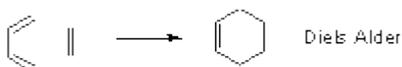
c) Conjugate Addition Reactions - Michael (1,4 Addition)



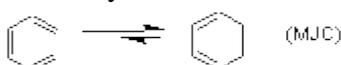
d) Reaction Of Alkenes, Alkynes And Aromatics

i) Pericyclic reactions:

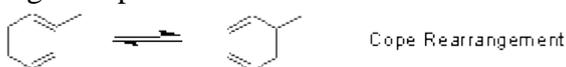
Cycloadditions



Electrocyclic reactions



Sigmatropic reactions



ii) Friedel Crafts and related reactions



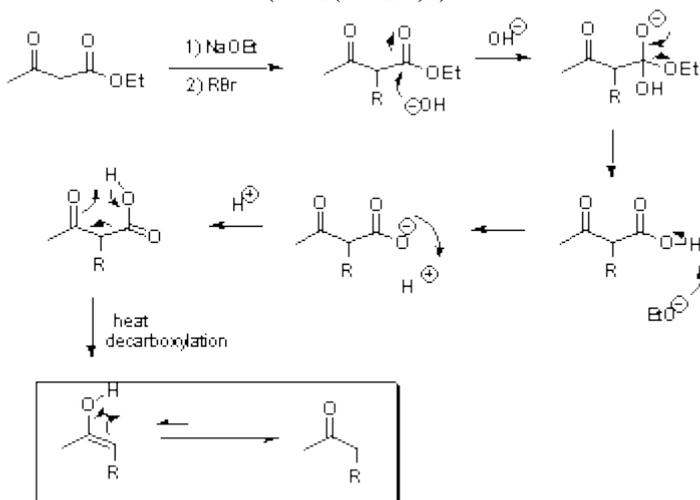
iii) Addition of carbenes to alkenes



Reactions of Active Methylene Compounds

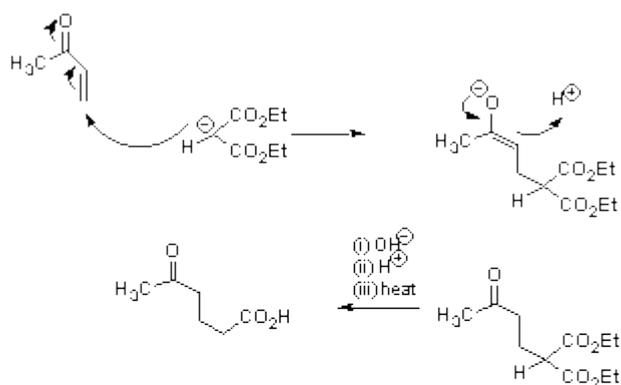
1) Carbanion Alkylation

Most important use is for preparation of ketones (from β -keto esters $\text{RCOCH}_2\text{CO}_2\text{Et}$) and of acids from malonic esters ($\text{CH}_2(\text{CO}_2\text{R})_2$).

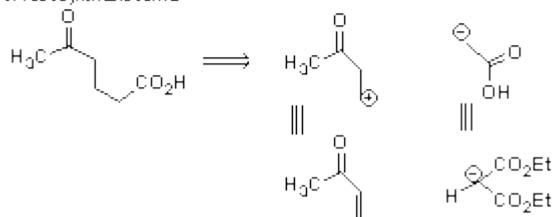


2) Michael Reaction with Active Methylene Compounds (Conjugate Addition Reaction)

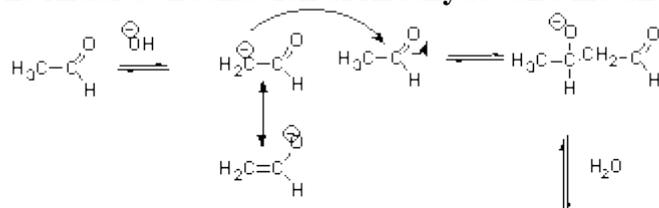
Carbanions derived from active methylene compounds react with α,β -unsaturated compounds by 1,4-(conjugate) addition known as Michael addition.



In retrosynthesis terms



The Aldol Condensation of Aldehydes and Ketones

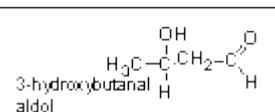


General for aldehydes and ketones with α -H

NB Reversible

Product favoured with RCH_2CHO

SM favoured with R_2CHCHO

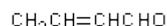


\uparrow -H₂O
 more vigorous
 conditions (heat)

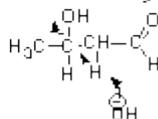
Reason for dehydration

1) Acidity of α -H

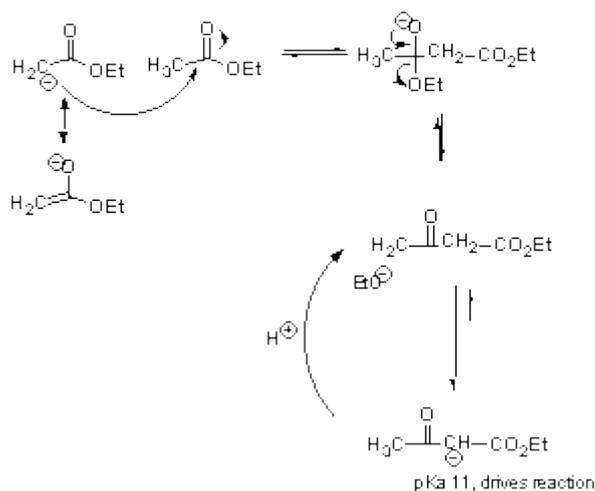
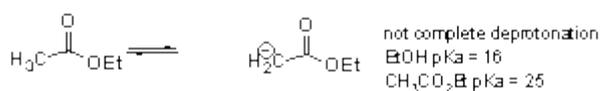
2) Stability of conjugated product



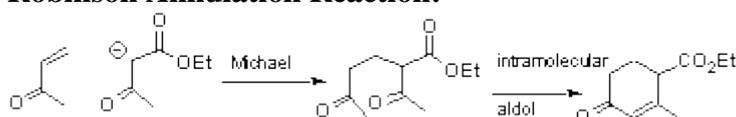
2-butenal



Claisen Condensation of Esters

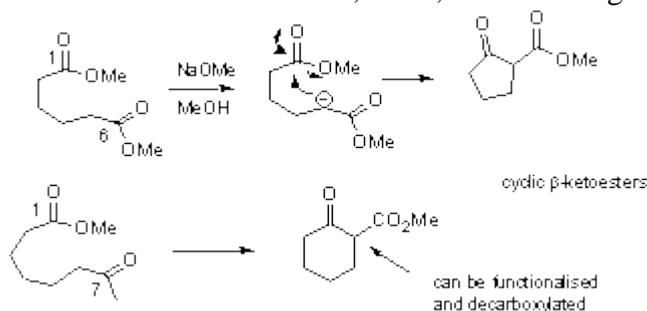


Robinson Annulation Reaction:

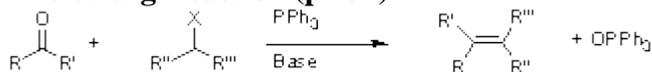


Intramolecular Claisen Condensations \blacklozenge The Dieckmann Cyclisation

Reaction works best with 1,6 or 1,7 diesters to give 5 or 6 membered rings.



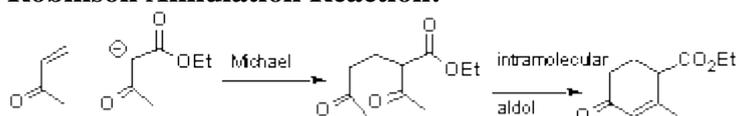
The Wittig Reaction (p 734)



Question 2. Discuss at least four such reactions where enolate ions are used for the purpose of skeleton building.

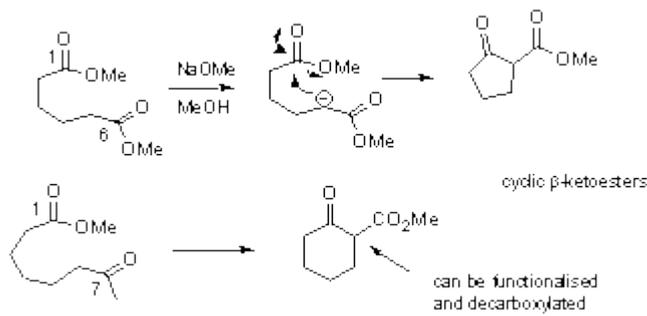
Answer:

Robinson Annulation Reaction:

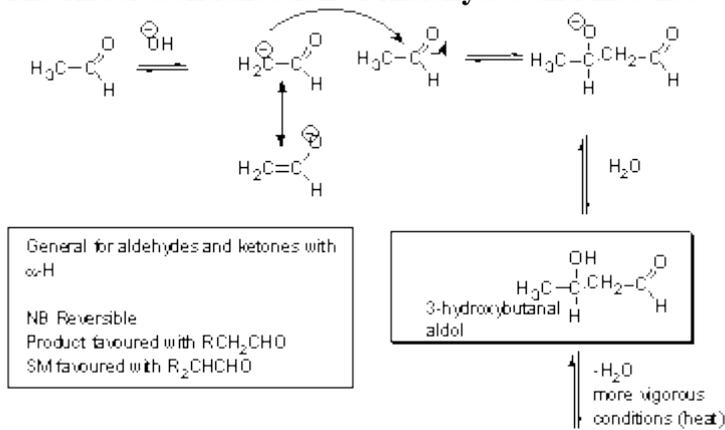


Intramolecular Claisen Condensations The Dieckmann Cyclisation

Reaction works best with 1,6 or 1,7 diesters to give 5 or 6 membered rings.



The Aldol Condensation of Aldehydes and Ketones



Claisen Condensation of Esters

