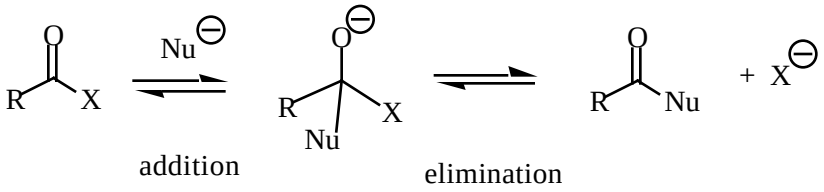
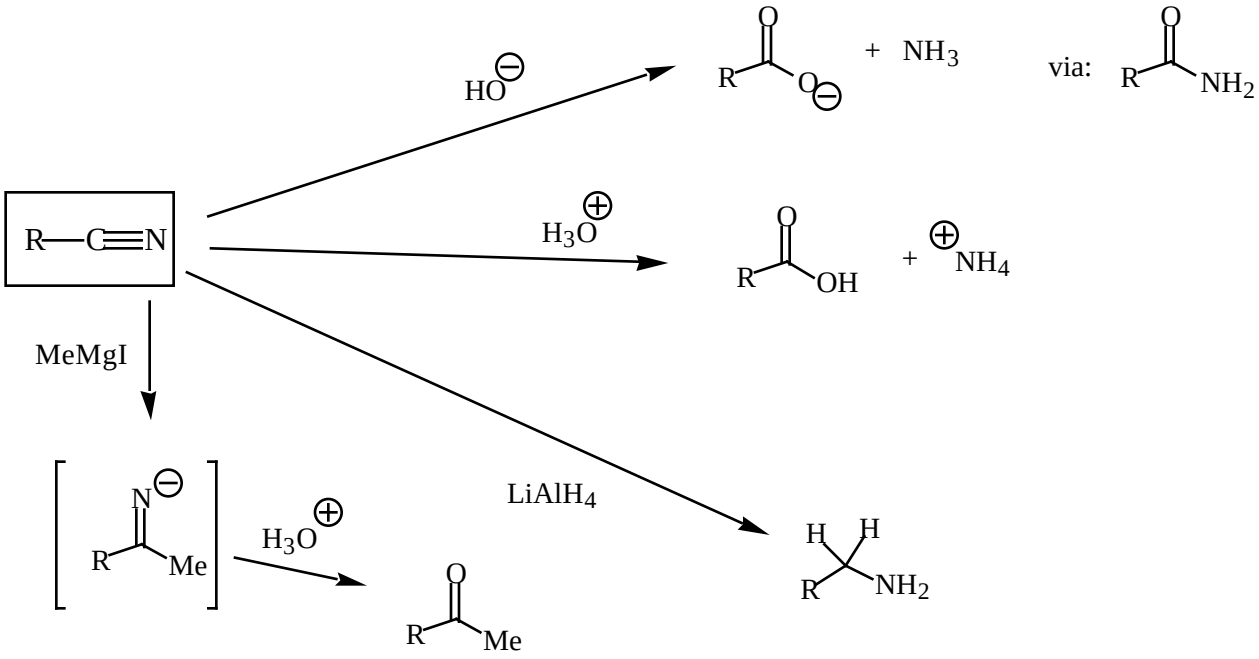
Exam II. One week from today, 7:30 pm 2.5 hr duration
Review sessions: Thursday evening
Sunday evening
Monday lecture

Addition/Elimination reactions Text Sec 20.4-20.7

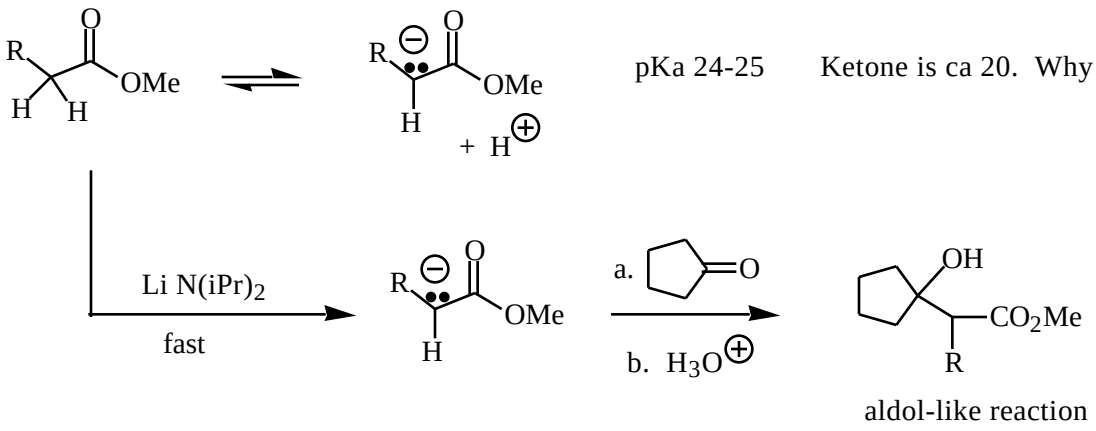


Nitriles: Text Sec 20.8



Write mechanisms: multistep

Enolate chemistry of esters: Aldol analog Text Sec 20.10

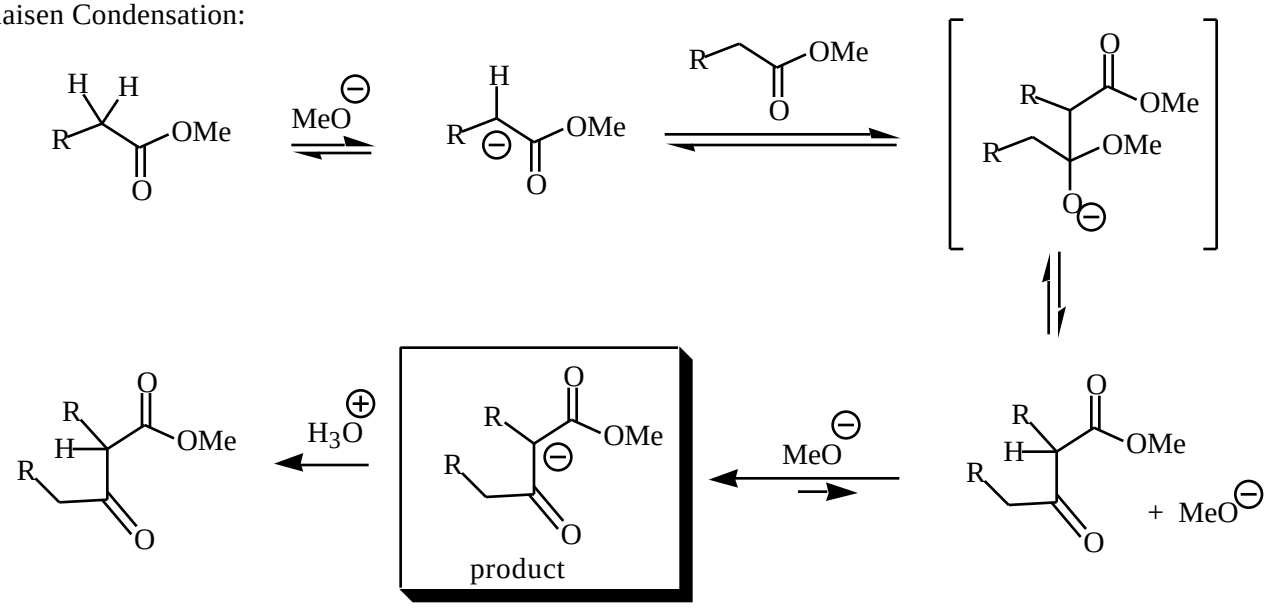


pKa 24-25 Ketone is ca 20. Why the difference?

aldol-like reaction

Equilibrium condensation reactions:

Claisen Condensation:

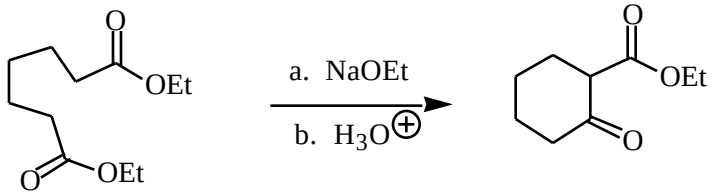


Driven by formation of an especially stabilized anion. General synthesis of β-ketoesters

This produces symmetical products--limited utility

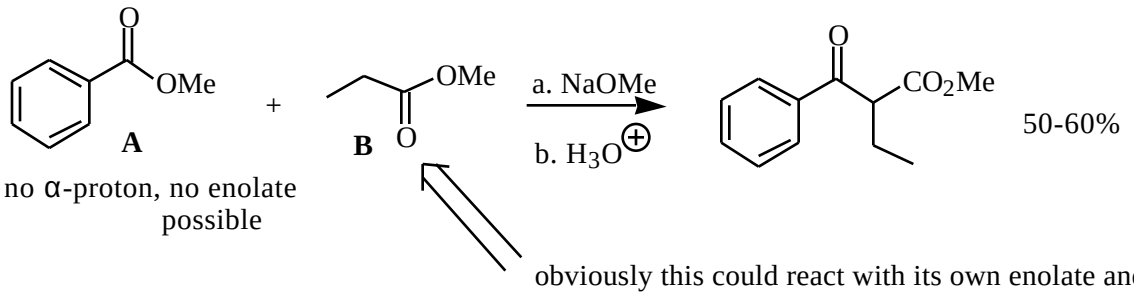
Special applications:

a. Intramolecular condensation: Dieckmann Condensation



5- and 6-membered rings

b. Crossed Aldol condensation.

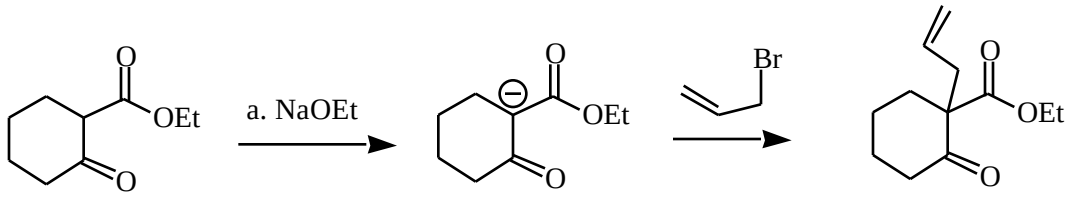


obviously this could react with its own enolate and it will. Favor the crossed reaction product by adding ester **B** slowly to a solution of ester **B** in base solution. Enolate of **B** forms and reacts with most abundant ester, **B**.

Think about crossed reactions of ketones with esters (to make β-diketones) **mechanism?**

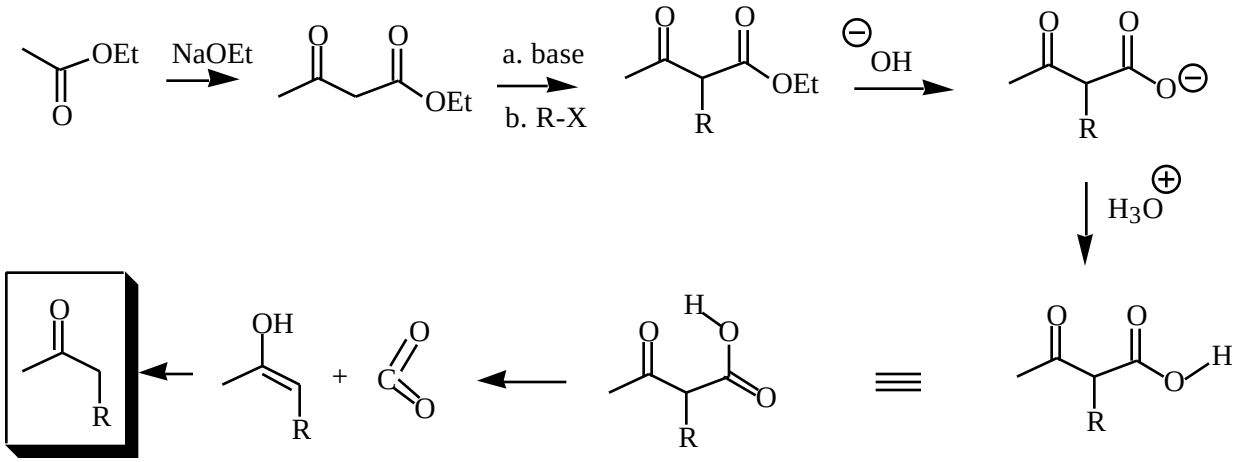
Self-aldol of ketones is fast but reversible; reaction with the ester by addition/elimination can drain the process is this direction.

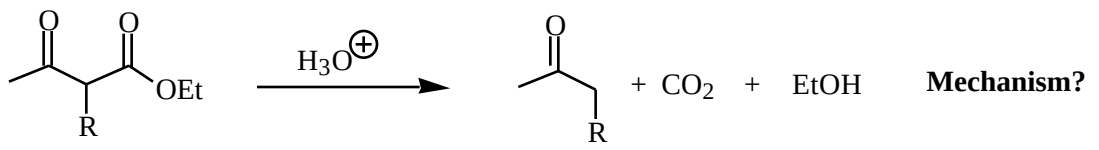
β-Keto esters are excellent substrates for alkylation: easily formed enolate with good S_N2 reactivity



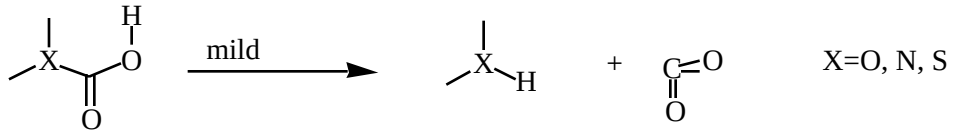
Particular value: The ester group, which allows construction and selective S_N2, can be removed easily:

DECABOXYLATION

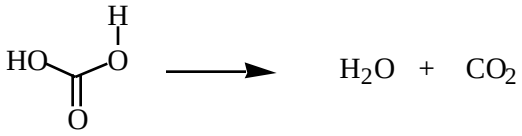




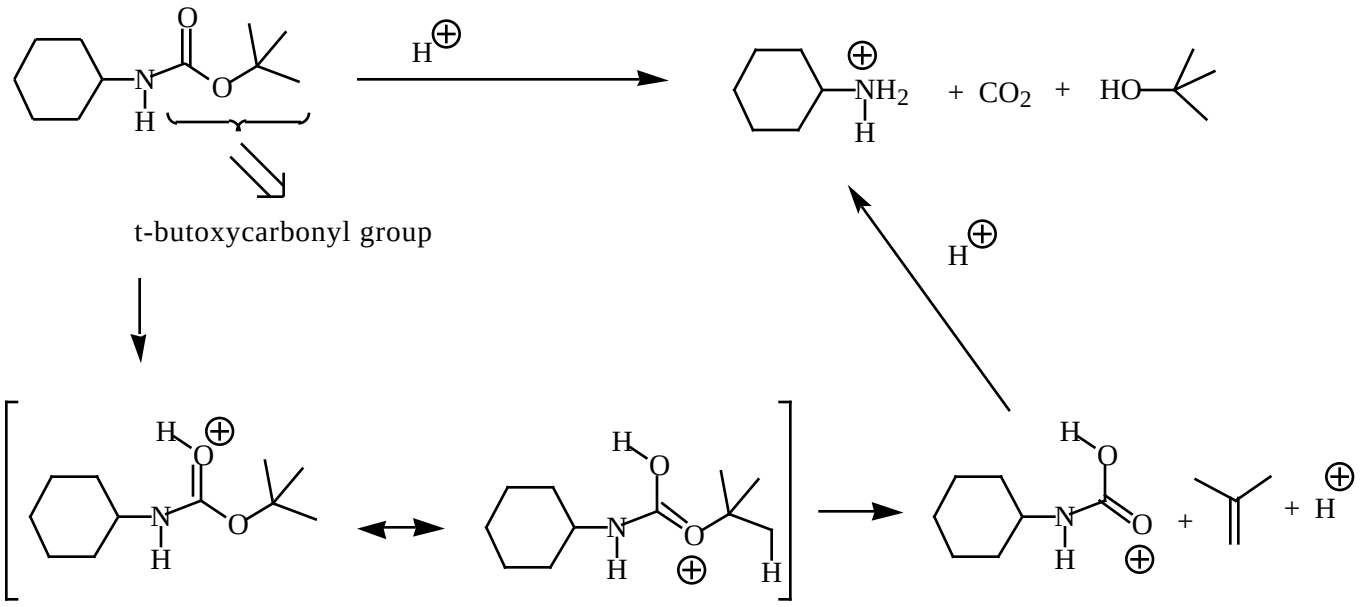
Decarboxylation is a general process:



e.g., carbonic acid is unstable:

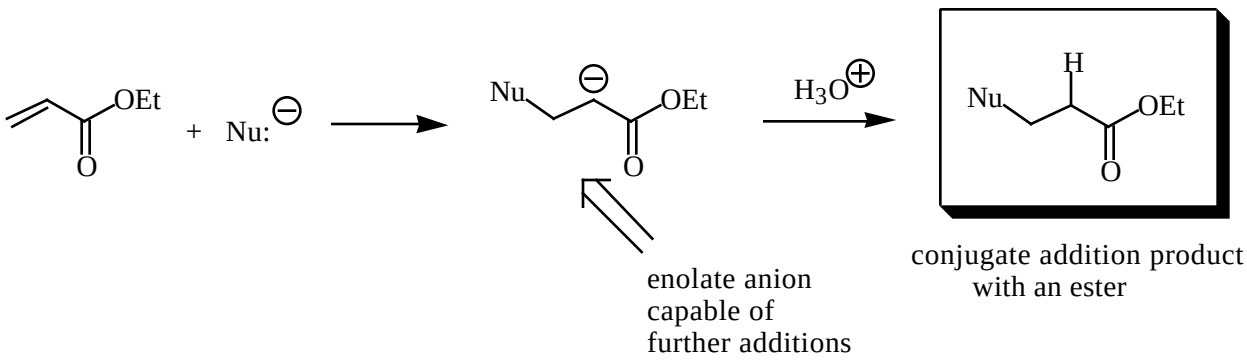


Protecting group for amines: modify reactivity so not interfere during other operations

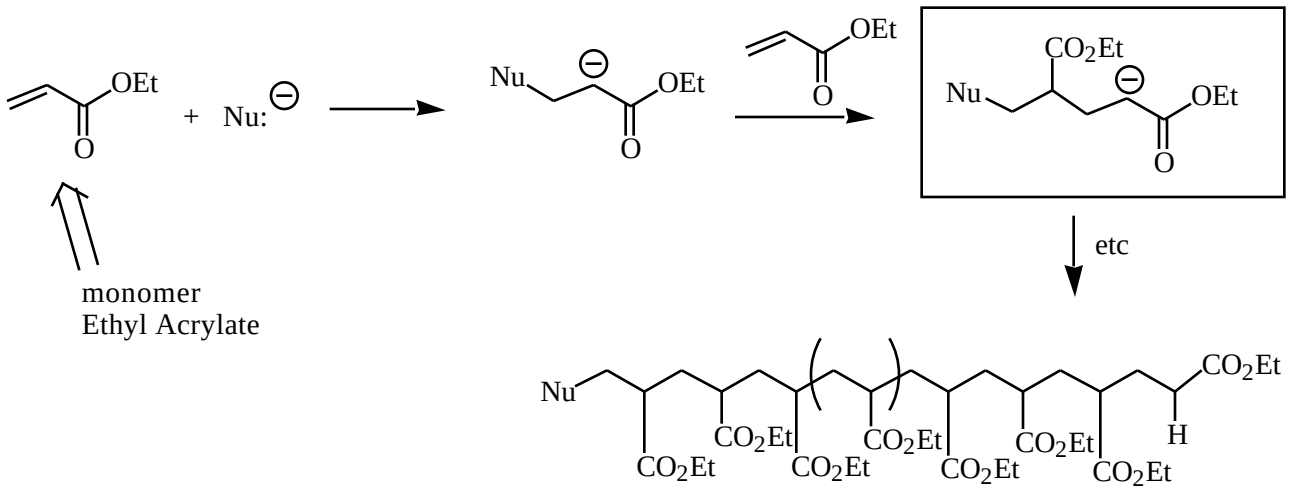


Special topics relating to esters and carbonyls:

Polymers: a. Addition polymers Recall the Michael reaction, conjugate addition



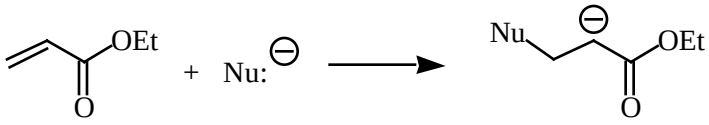
Anionic Polymerization:



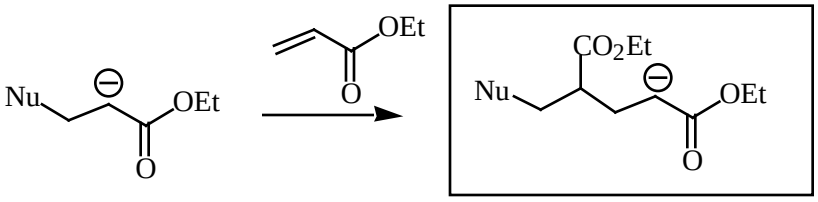
acrylic polymers

Classify steps:

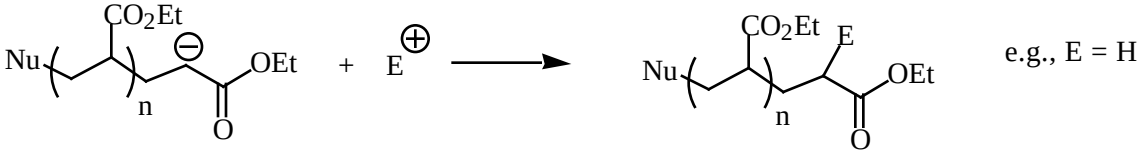
a. Initiation (creates relevant anion)



b. Chain carrying (converts anion to anion)



c. Termination (quenches the anion)

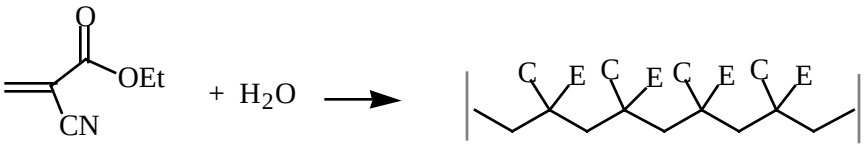


e.g., E = H

any process which does not generate an anion/nucleophile

Polymers have strong intermolecular attractions: fibers, glues, plastic materials--
depends on chain length, side chains

Super glue:

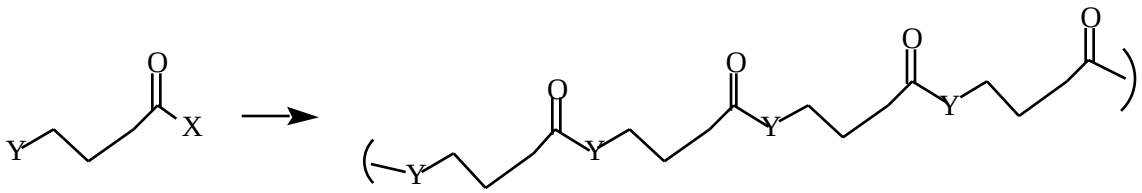


ethyl cyanoacrylate

C = CN; E = CO_2Et

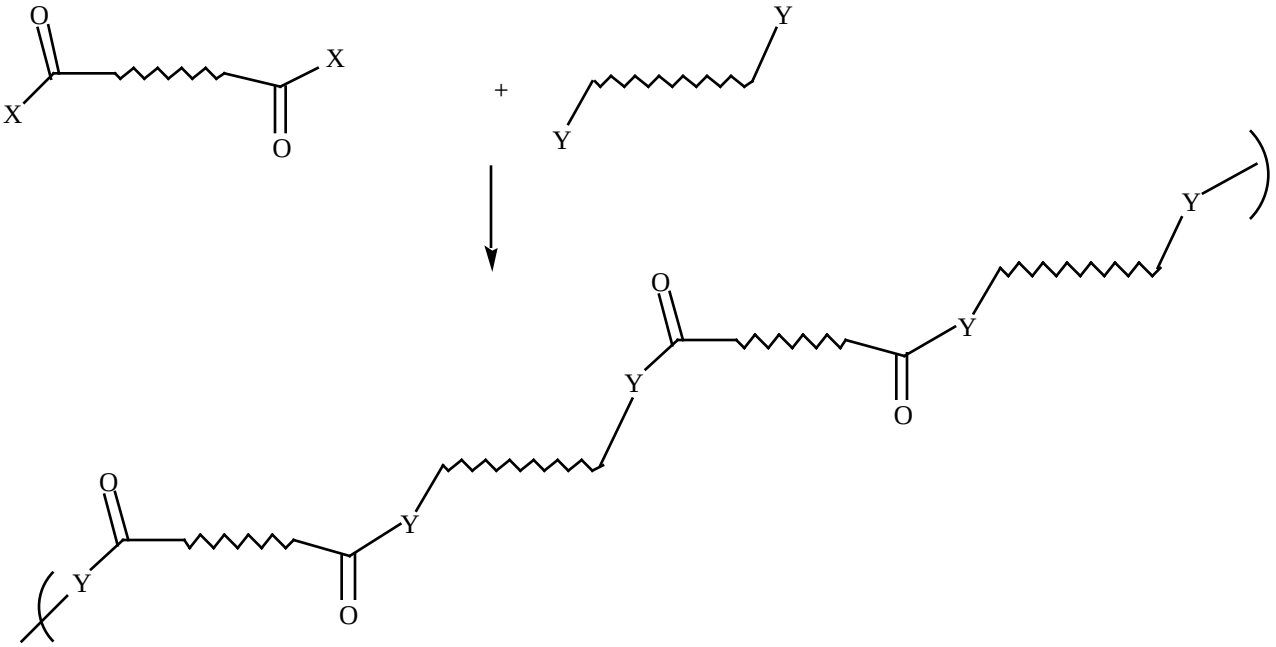
Polymerization of Bifunctional Acyl Derivatives:

Homopolymer:

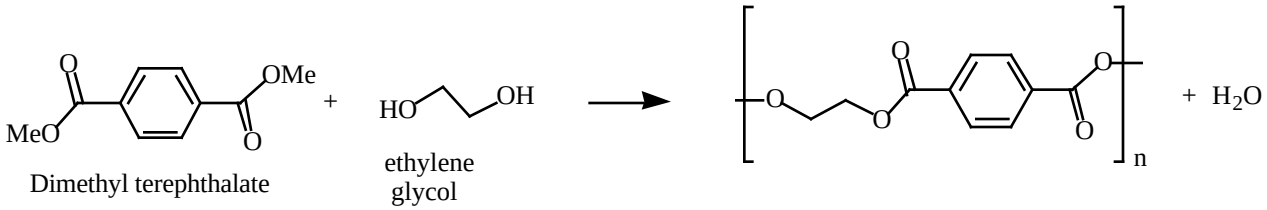


Y = nucleophile (-OH, $-NH_2$, etc) X = leaving group such as Cl, OMe, etc

Alternating Copolymer:



Example: A Polyester Dacron, Mylar

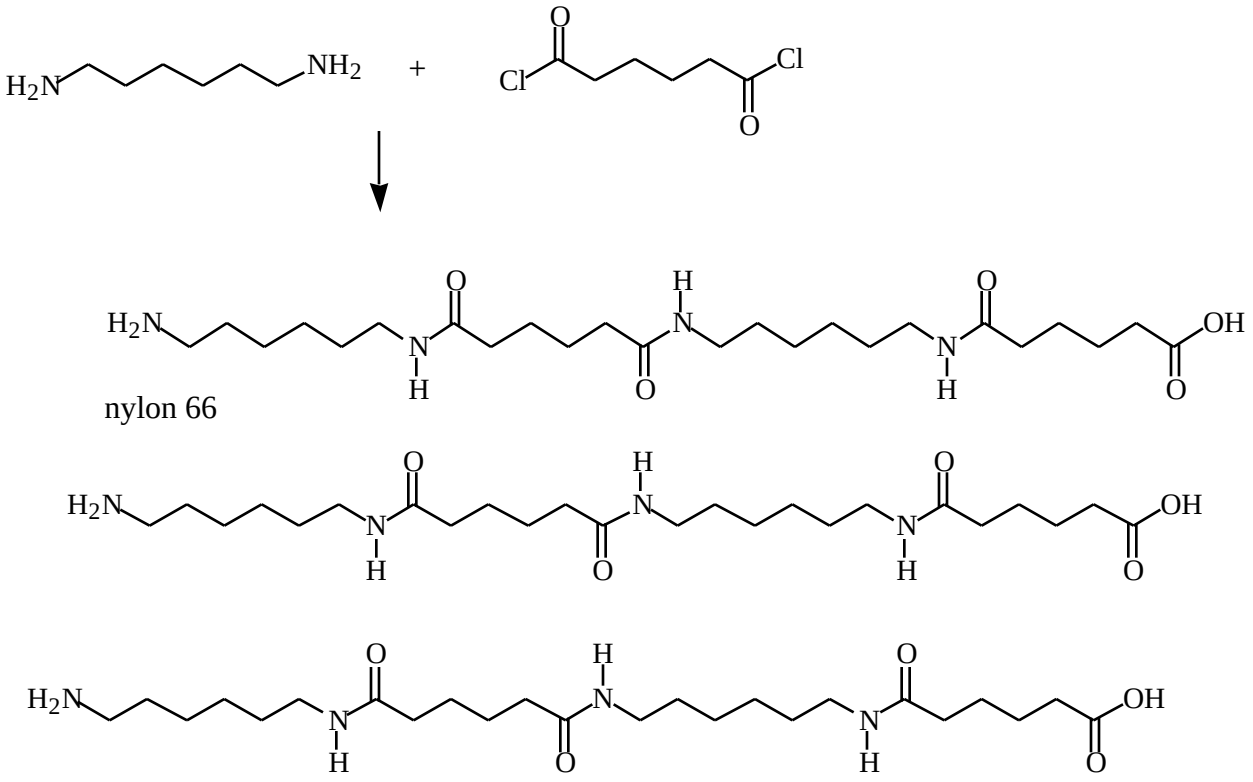


Dimethyl terephthalate

ethylene glycol

Example: Polyamide

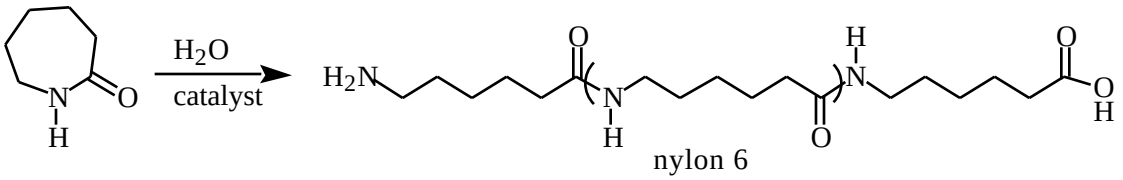
Alternating copolymer of amides NYLON:



nylon 66

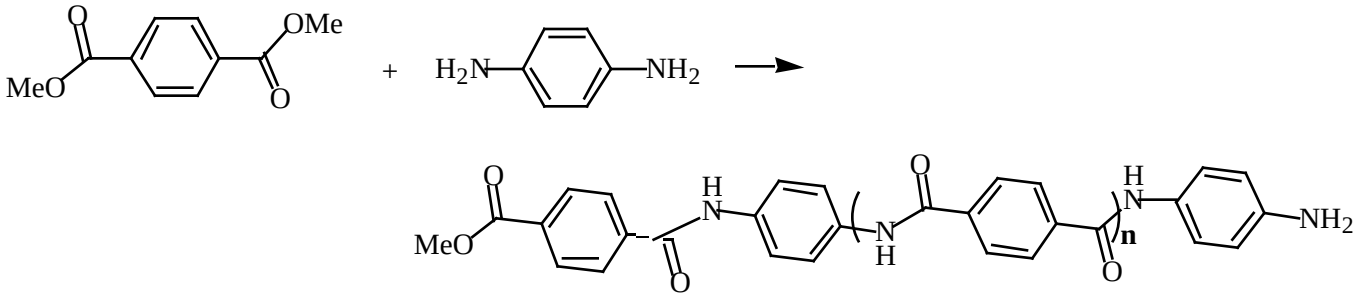
Synthesis: adipoyl chloride in HEXANE (non-polar, non-nucleophilic, lighter than water)
1,6-diaminohexane in water/base

Note:

caprolactam 

nylon 6

Mechanism?



Ketenes

Thermal elimination

Thiols and thiol esters: biologtical esterification (sorrel p 933

Wittig reaction
Properties of the acyl compounds with focus on amides