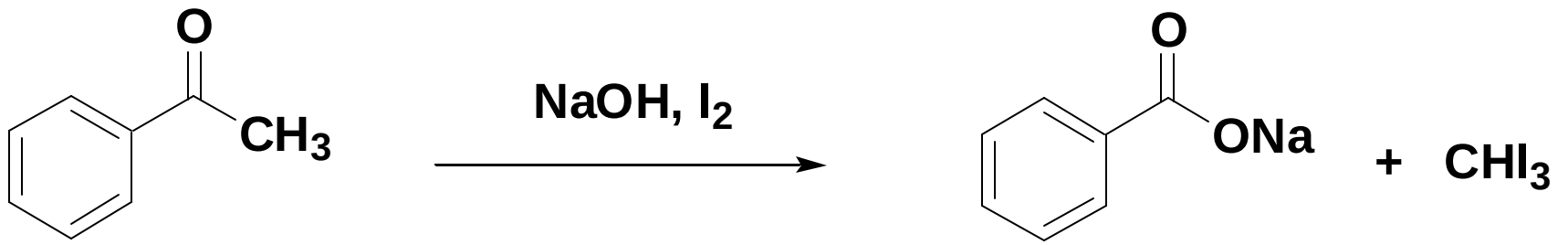
Lecture 24 – Chapter 18 : Reactions involving Enolates

- Enolates reacting with electrophiles
- Deuteration at α-carbon
- The aldol condensation
- Mixed aldol reactions
- Conjugation in aldehydes and ketones
- Conjugate addition

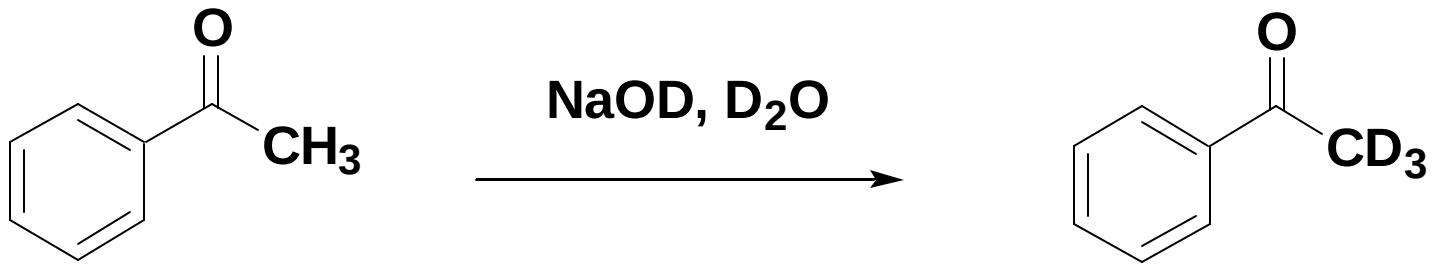
Reactions involving enolates – the iodoform reaction



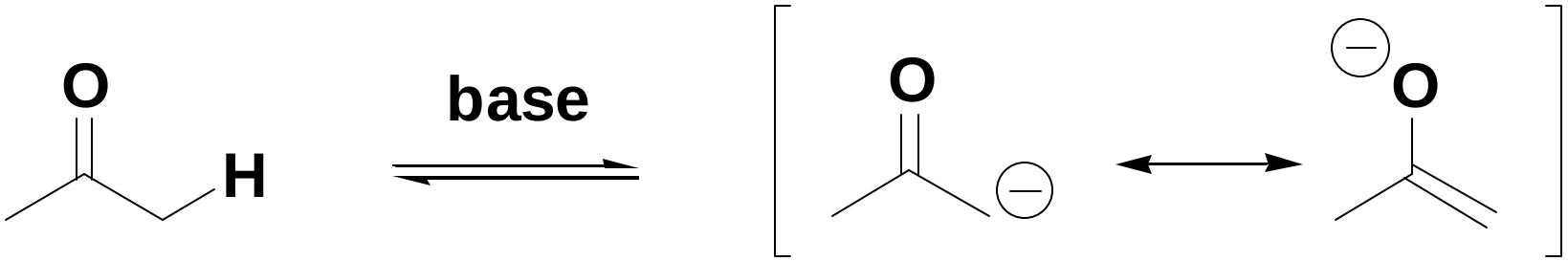
A methyl ketone

iodoform

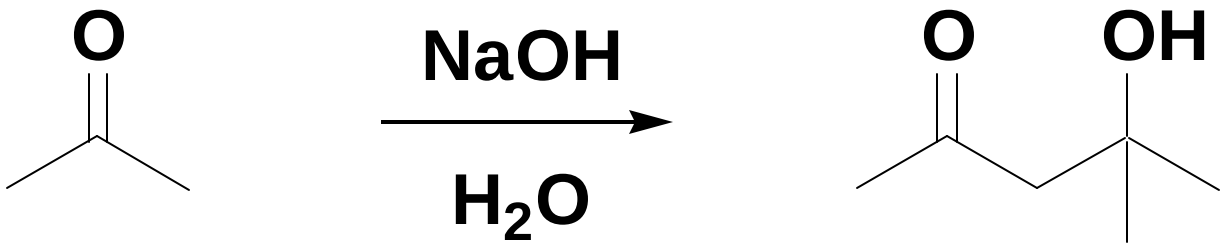
a-Deuteration



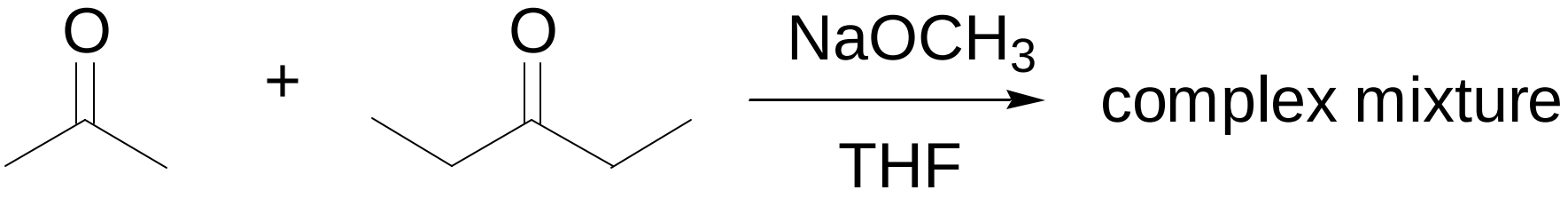
The aldol condensation



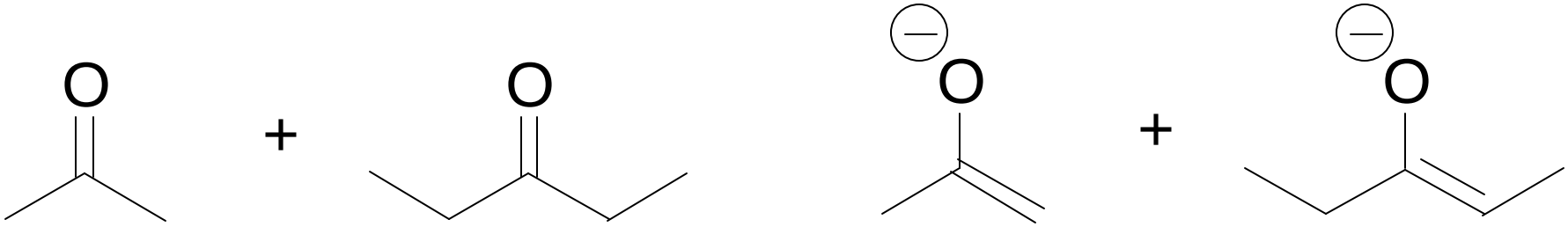
When appropriate base is used, both ketone and enolate present in solution, this leads to the aldol reaction



Mixed (crossed) aldol reactions

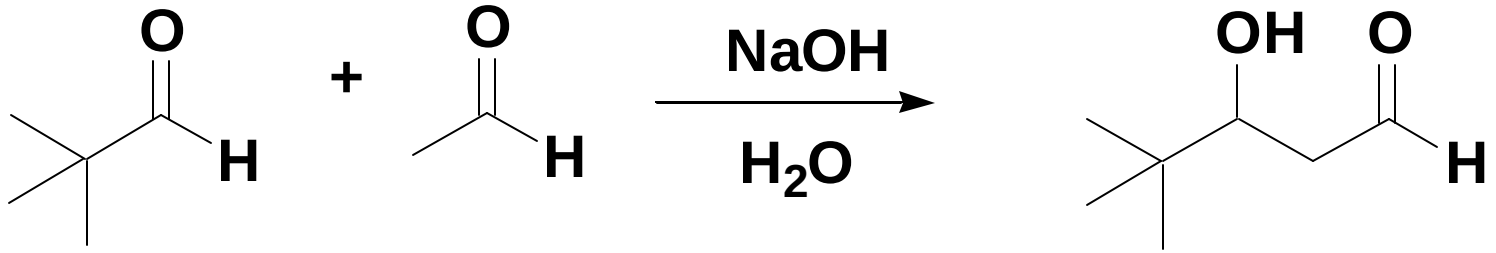


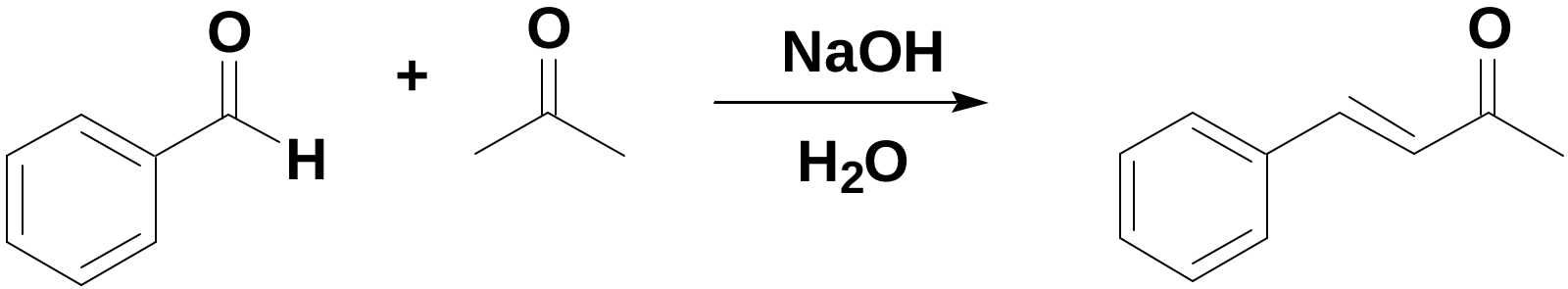
2 enolizable substrates leads to multiple products



all present in solution at same time

Have to use 1 non-enolizable substrate:

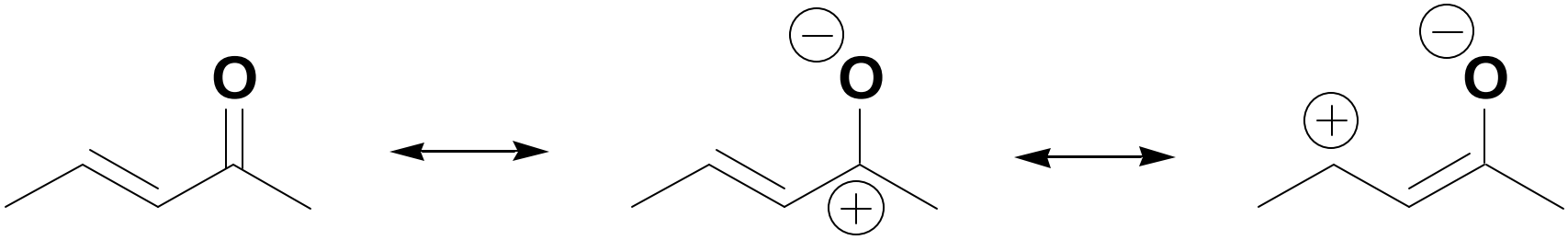




83%

Elimination of H_2O common when conjugation results, can also be induced by heating the reaction mixture

Conjugation in a,b-unsaturated carbonyl compounds



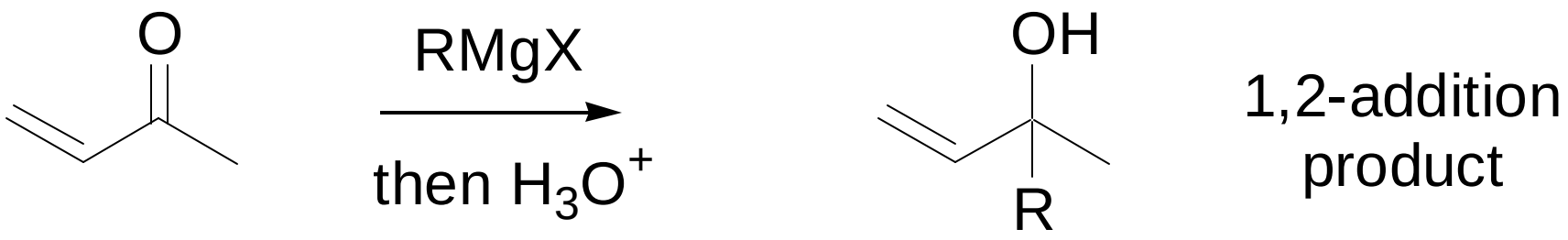
Carbonyl carbon and b-carbon have positive character

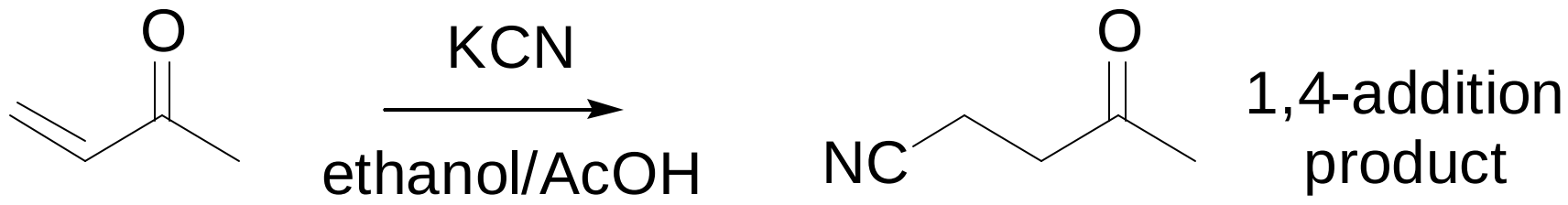
Acrolein

Figure 18.5

Pi system is completely delocalized

Conjugate addition – 1,2- vs 1,4-addition





More reactive nucleophiles (e.g. RMgX) attack the most +ve C i.e. the carbonyl carbon. These reactions are usually irreversible.

Softer nucleophiles undergo reversible addition and lead to the more stable (thermodynamically favoured) 1,4-addition product.

Monday

- The Michael reaction
- The Robinson annulation
- Alkylation of enolates

Lab report due today