CHEM 342 – Lecture 12 *12/03/15*

Overheads: - Today's Outline

Recap Tuesday:

Enolates:

1) C-alkylation *vs* O-alkylation

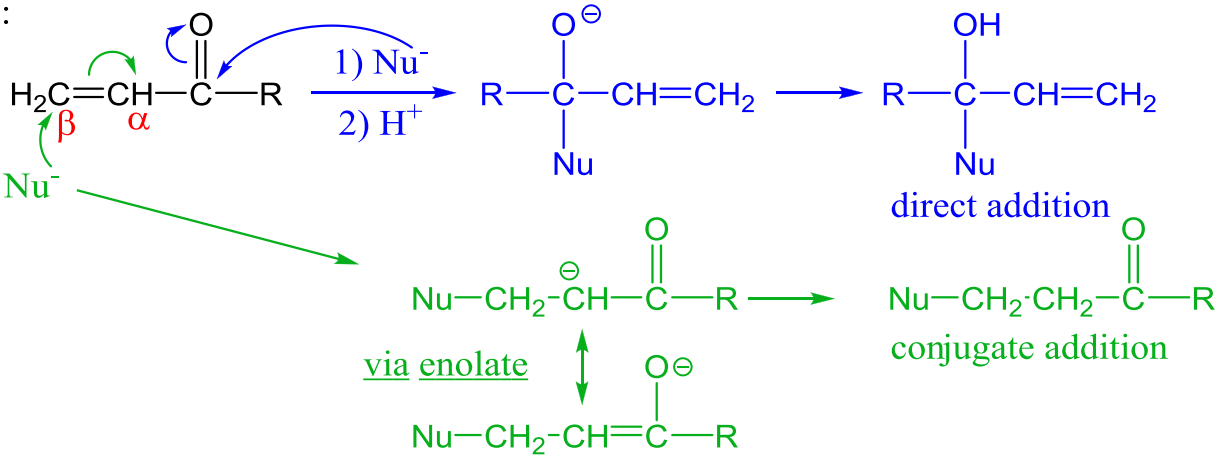
C-alkylation	O-alkylation
"bound" enolate	"free enolate"
-Li, less polar solvents	- Na, K, chelating solvents / crown ethers
- LG = halide	- LG = sulfonate

2) kinetic *vs* thermodynamic

kinetic	thermodynamic
- least sub	- most sub = most stable
- big base	- small base
- cold	- hot

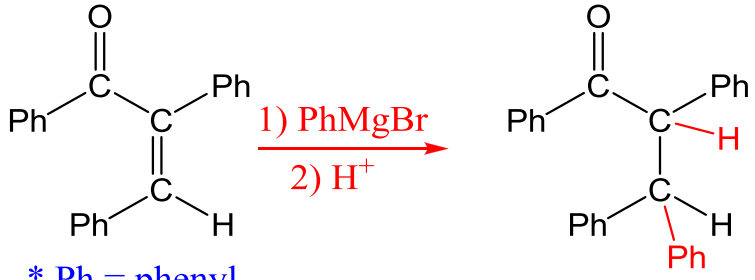
Addition to α,β-unsaturated carbonyls

In general:



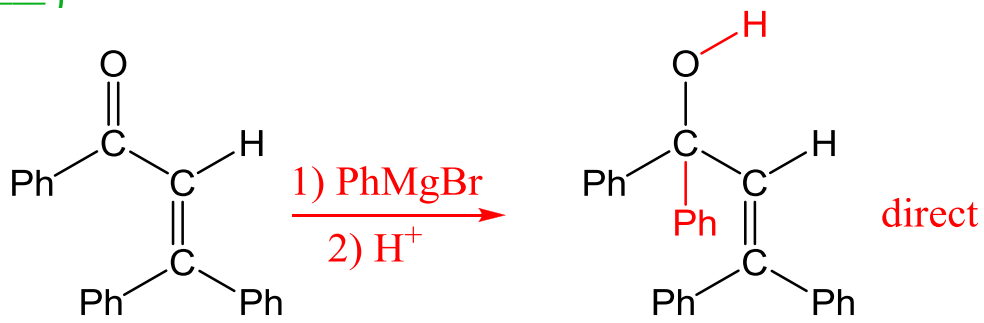
Direct vs Conjugate Addition: depends on Nu^-

1) Nu^- = Grignard – usually adds conjugate

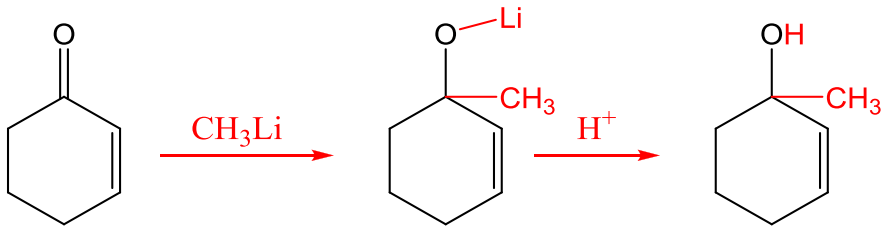


* Ph = phenyl

unless β-C is crowded:

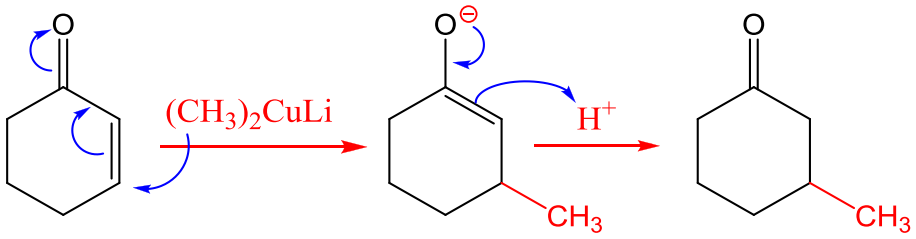


2) Nu^- = R-Li – almost always adds direct



3) Nu^- = organocuprate R-Cu< – always adds conjugate

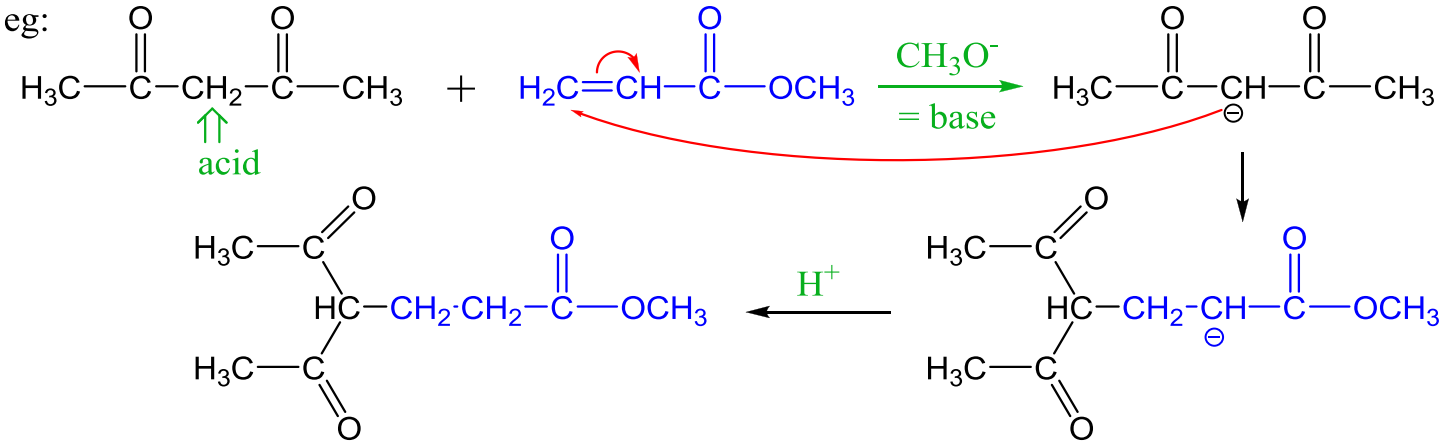
$2CH_3Li + CuCl \rightarrow (CH_3)_2CuLi + LiCl$



complementary

4) Nu^- = enolate – usually adds conjugate **Called Michael Reaction

eg:



Aldol Reaction: enolate adds to C=O of another molecule