Nucleophilic Addition Of Hard Anions To Aldehydes And Ketones

from chapter(s) _____ in the recommended text

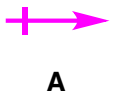
A. Introduction

B. Types Of Additions To Carbonyls

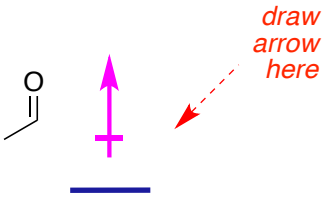
Polarity Of Carbonyls

.

positively polarized.

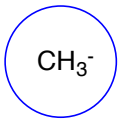


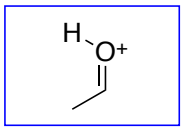
A



to carbonyl *carbons*
oxygen.

Reactivity Of Nucleophiles And Carbonyls At Different pH Values





more reactive
more reactive than ones that are not.

hard because
are likely to
cannot be used

completely wrong to show
neutral or basic conditions.

In the second edition of the book a somewhat ambiguous question has been changed from:

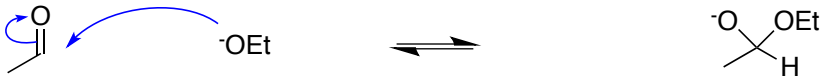
Additions of reactive basic anions to carbonyl compounds *can/cannot* be reversible if the anion involved is very stable.

to:

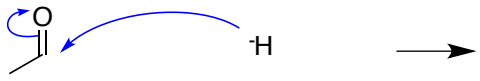
Additions of unstable, reactive, basic anions to carbonyl compounds tend to be *reversible / irreversible*.

the answer is *irreversible*.

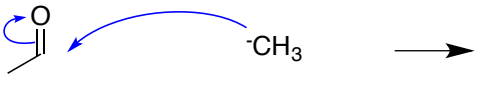
Formation Of Tetrahedral Intermediates



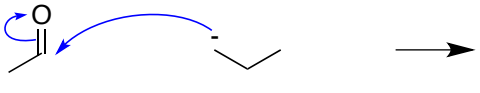
tetrahedral intermediate



tetrahedral intermediate



tetrahedral intermediate



tetrahedral intermediate

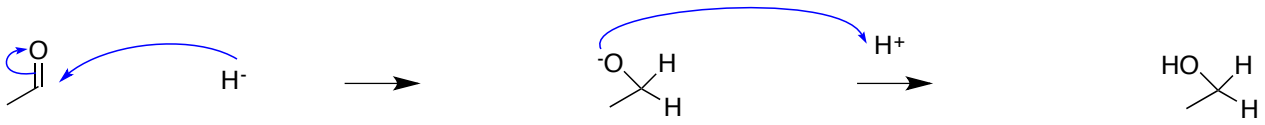
sp^3 hybridized.
give *alcohols*.
(this is *kinetics*),
(*thermodynamics*).

one *C–O* bond(s)
one bond(s)
the *starting materials*.
it *will* be
ie *irreversible* addition.

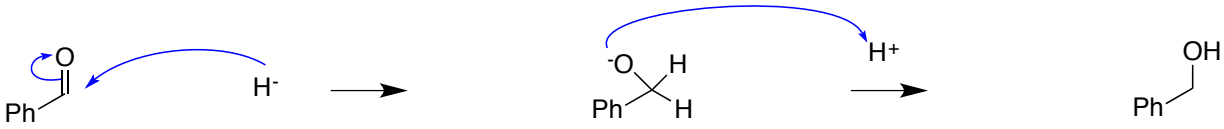
Cl^- Br^- CN^-	MeO^-	Me^- Ph^- CH_2CH^-
relatively stable		*relatively unstable*

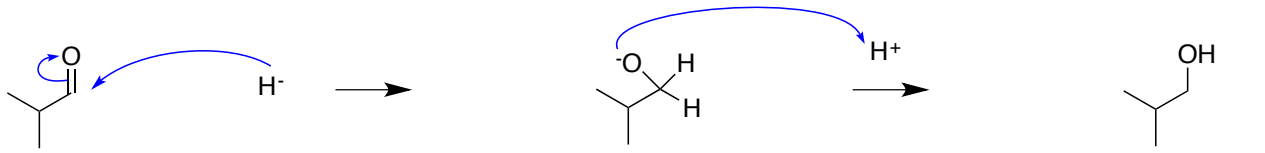
reversibly to ketones

C. Reactions of Aldehydes And Ketones With Hydridic Reducing Agents



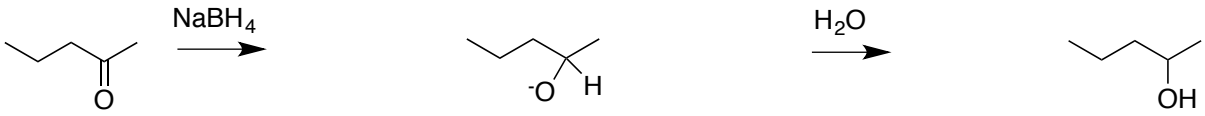
tetrahedral intermediate *product*

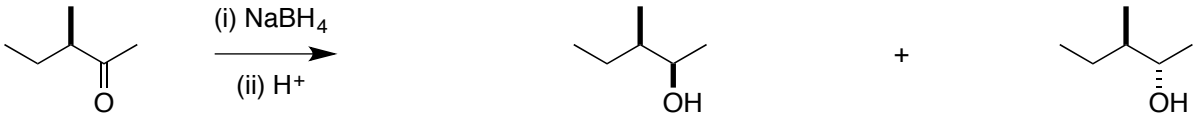




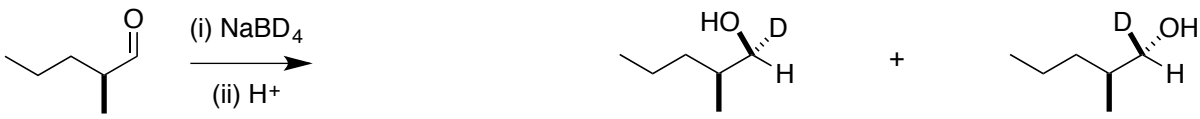
$NaBH_4$	NaH	$LiAlH_4$
name: Sodium Borohydride	*Sodium Hydride*	*Lithium Aluminium Hydride*
nucleophilc	*basic*	*nucleophilc*

does not do



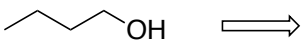


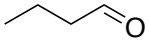
two diastereomers

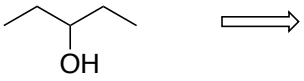


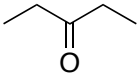
two diastereomers

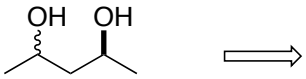
reduction processes.

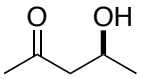


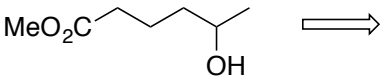


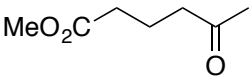






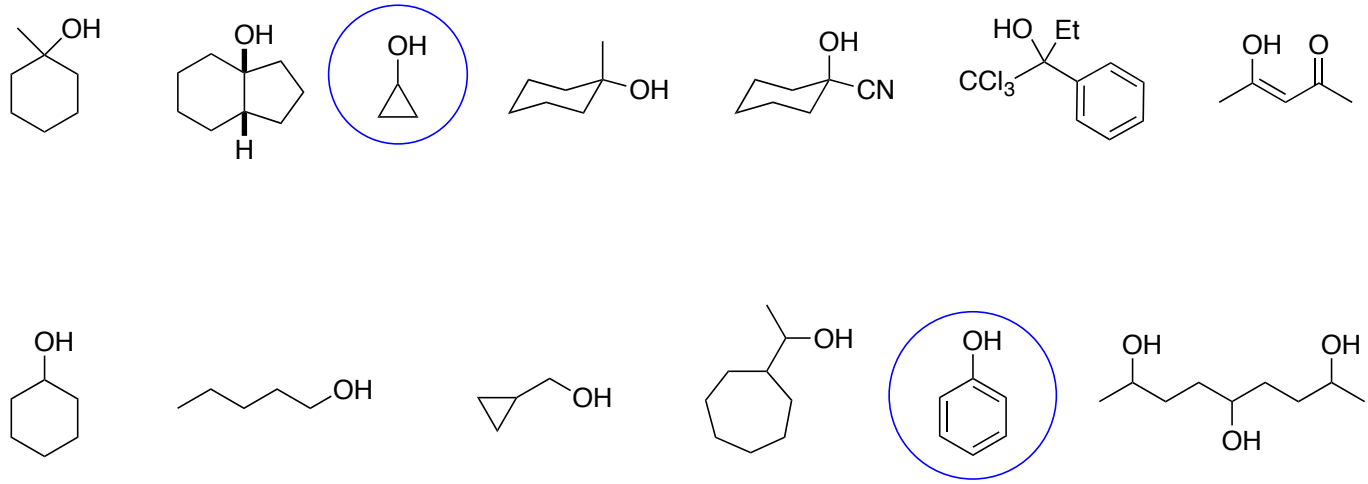






because:

Lithium aluminium hydride can reduce ester to alcohol, but sodium borohydride cannot.



D. Addition Of Carbanions

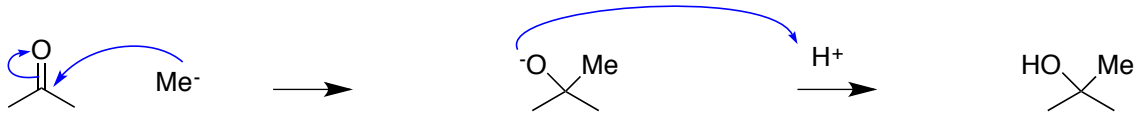
reactive

carbonyls *irreversibly*.

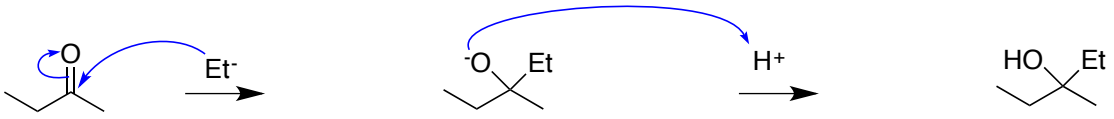
is *stronger* than

under *anhydrous* conditions.

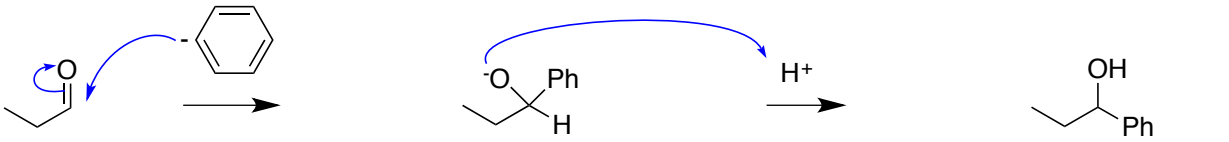
alkoxide *does not*



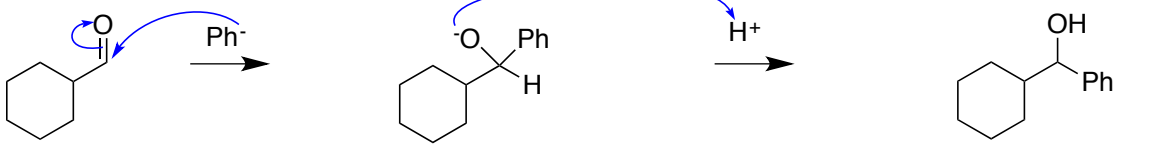
tetrahedral intermediate



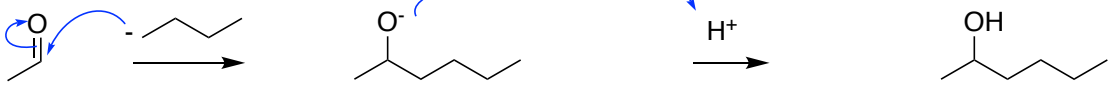
tetrahedral intermediate



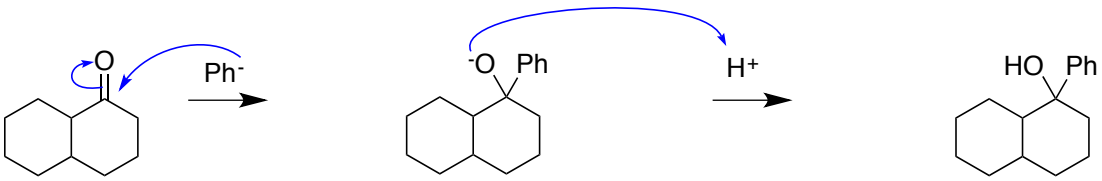
tetrahedral intermediate



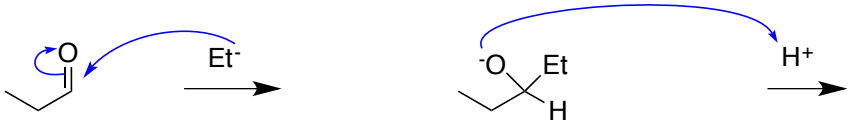
tetrahedral intermediate



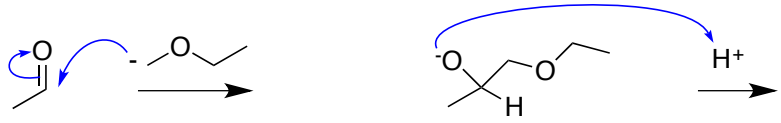
tetrahedral intermediate



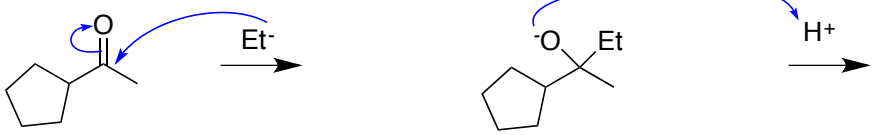
tetrahedral intermediate



tetrahedral intermediate



tetrahedral intermediate

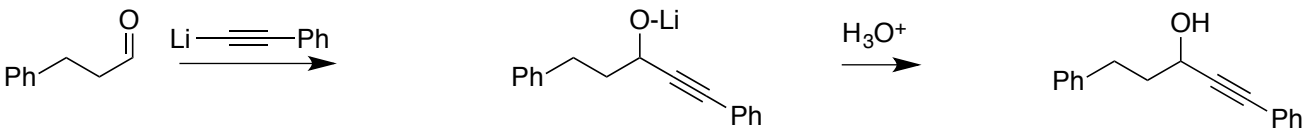


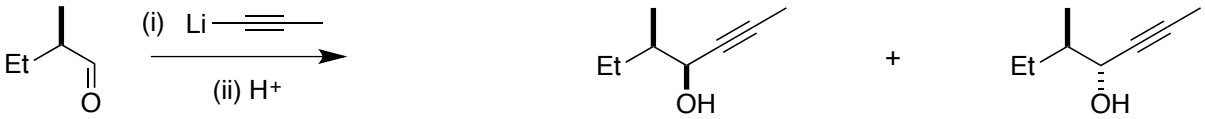
tetrahedral intermediate

E. Reactions Of Carbonyl Compounds With Acetylide Anions

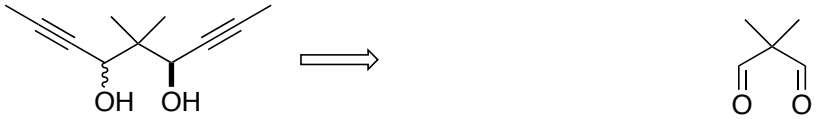
NEt_3 $NaNH_2$ $MeMgBr$ HO^- LiN^iPr_2 $LiBu$ Na_2CO_3

secondary or tertiary





two diastereomers



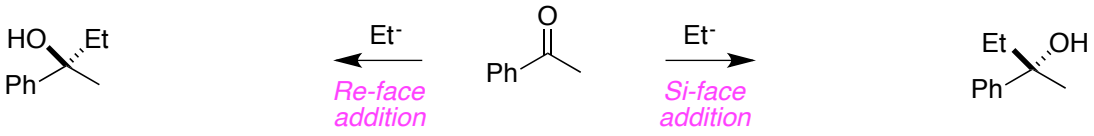
two diastereomers

F. *Si* And *Re* Faces Revisited

enantiomers.

Re-face attack

Si -face attack.



(*R*)-Alcohols *are not*
(*S*)-alcohols *are not*