# Nucleophilic Addition Of Hard Anions To Aldehydes And Ketones

from chapter(s)	in the recommended te	xt
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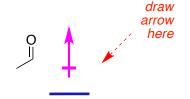
## A. Introduction

## **B. Types Of Additions To Carbonyls**

**Polarity Of Carbonyls** 

positively polarized.





to carbonyl *carbons* oxygen.

## **Reactivity Of Nucleophiles And Carbonyls At Different pH Values**



 $NH_3$ 





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

sp³ hybridized. give alcohols. (this is kinetics), (thermodynamics). one C-O bond(s) one bond(s)

the starting materials.

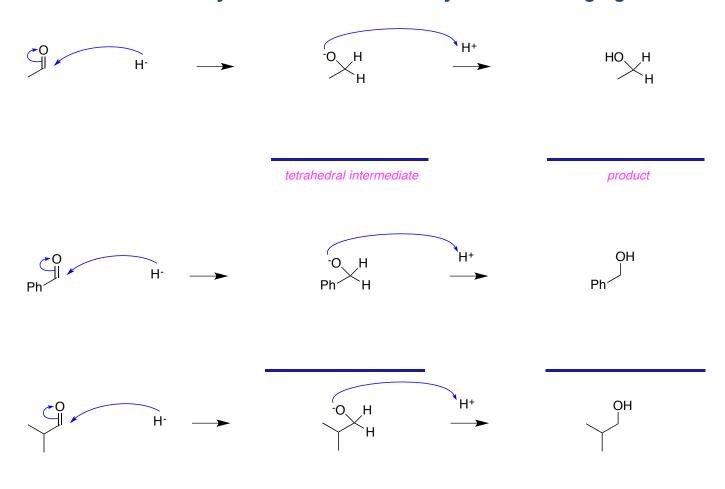
it will be

ie irreversible addition.

Cl- Br- CN-	MeO <sup>-</sup>	Me⁻ Ph⁻ CH <sub>2</sub> CH⁻
relatively stable		relatively unstable

reversibly to ketones

# C. Reactions of Aldehydes And Ketones With Hydridic Reducing Agents



$$H$$
  $OH$   $H$ 

NaBH<sub>4</sub>  $LiAlH_4$ NaH name: Sodium Borohydride Sodium Hydride Lithium Aluminium Hydride nucleophilc nucleophilc basic

does not do

### two diastereomers

two diastereomers

## 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.

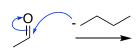
alkoxide does not

tetrahedral intermediate

### tetrahedral intermediate

### tetrahedral intermediate

## tetrahedral intermediate

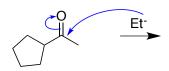




### tetrahedral intermediate

## tetrahedral intermediate

### tetrahedral intermediate



# E. Reactions Of Carbonyl Compounds With Acetylide Anions

 $LiN^{i}Pr_{2}$ LiBu NEt<sub>3</sub> NaNH<sub>2</sub> MeMgBr HO- $Na_2CO_3$ 

## secondary or tertiary

$$H_2CO$$
  $(i) H_2C_2$ , excess NaH  $(ii) H^+$   $HO$ 

two diastereomers

$$\stackrel{\circ}{\downarrow}$$



two diastereomers

## F. Si And Re Faces Revisited

enantiomers.

Re-face attack

Si -face attack.

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