Nucleophilic Addition Of Hard Anions To Aldehydes And Ketones

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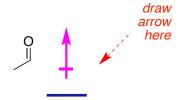
A. Introduction

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.

cannot be reversible.

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.

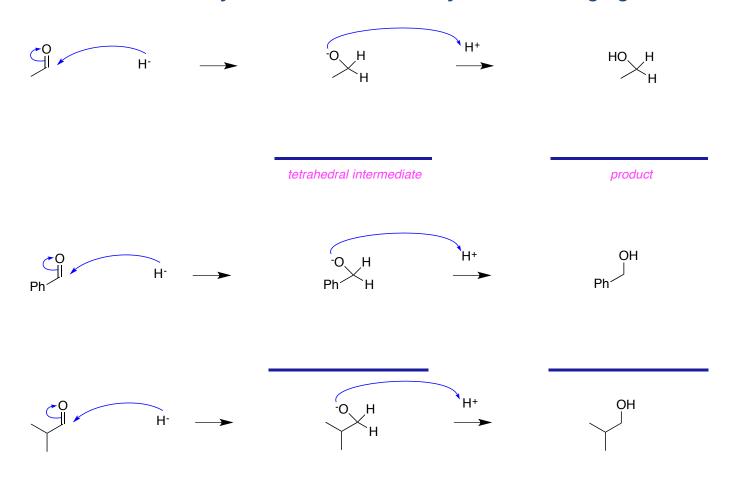
it will be

ie irreversible addition.

Cl- Br- CN-	MeO-	Me ⁻ Ph ⁻ CH ₂ CH ⁻
relatively stable		relatively unstable

reversibly to ketones

C. Reactions of Aldehydes And Ketones With Hydridic Reducing Agents



$$H$$
 OH H

$$H^{+}$$
 \to H^{+} \to \to \to

does not do

two diastereomers

two diastereomers

$$MeO_2C$$
 \longrightarrow MeO_2C \bigcirc \bigcirc

because:

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

D. Addition Of Carbanions

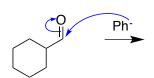
carbonyls irreversibly. is *stronger* than under anhydrous conditions.

alkoxide does not

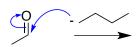
tetrahedral intermediate

tetrahedral intermediate

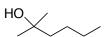
tetrahedral intermediate



tetrahedral intermediate



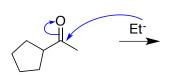


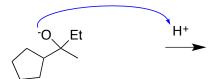


tetrahedral intermediate

tetrahedral intermediate

tetrahedral intermediate





E. Reactions Of Carbonyl Compounds With Acetylide Anions

MeMgBr $\text{LiN}^{\text{i}}\text{Pr}_2$ NEt_3 LiBu Na_2CO_3 HO⁻

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