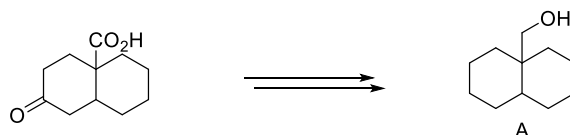


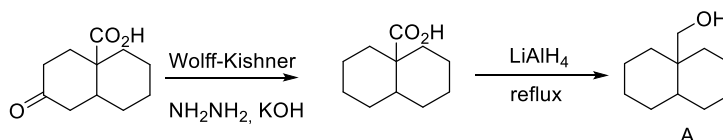
Solutions to Problems – Set 6: Carbonyl compounds (part II)

Problem 1

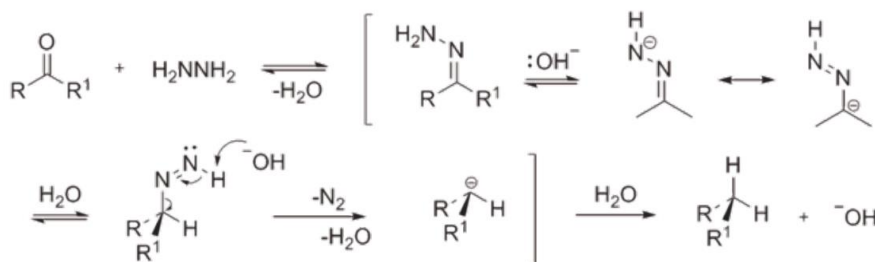
Give possible synthetic pathway for compound **A** from ethyl 2-oxodecahydronaphthalene-4a-carboxylate as well the detailed mechanism of these transformations (think about the reduction method seen in class)



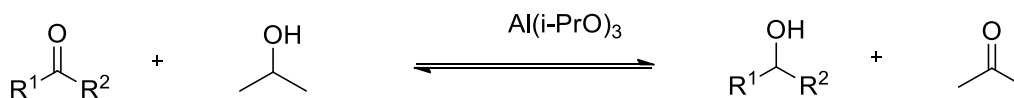
Solution



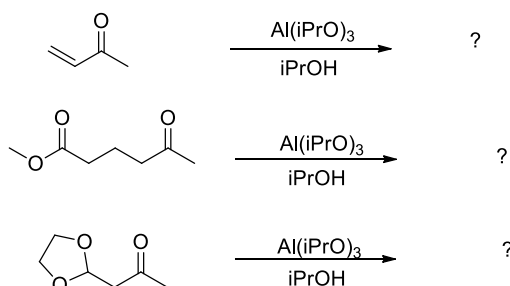
Mechanism of Wolff-Kishner reaction



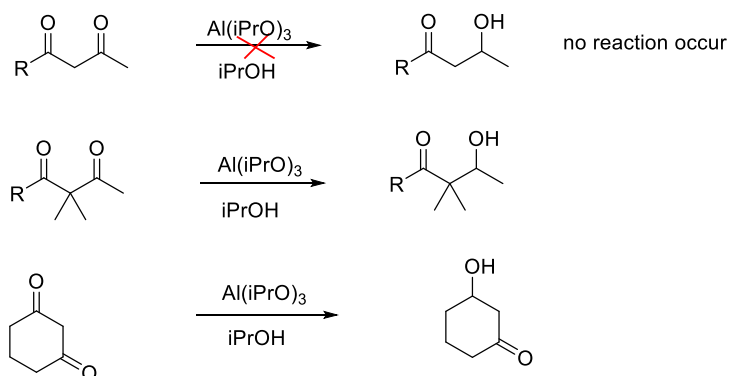
Problem 2 Meerwein-Ponndorf-Verley Reduction



- What is the name of reverse reaction, the oxidation of alcohol to aldehyde or ketone?
- Give detailed mechanism, draw clearly the transition state?
- How to move the equilibrium in desired direction?
- Give the product for following transformations?



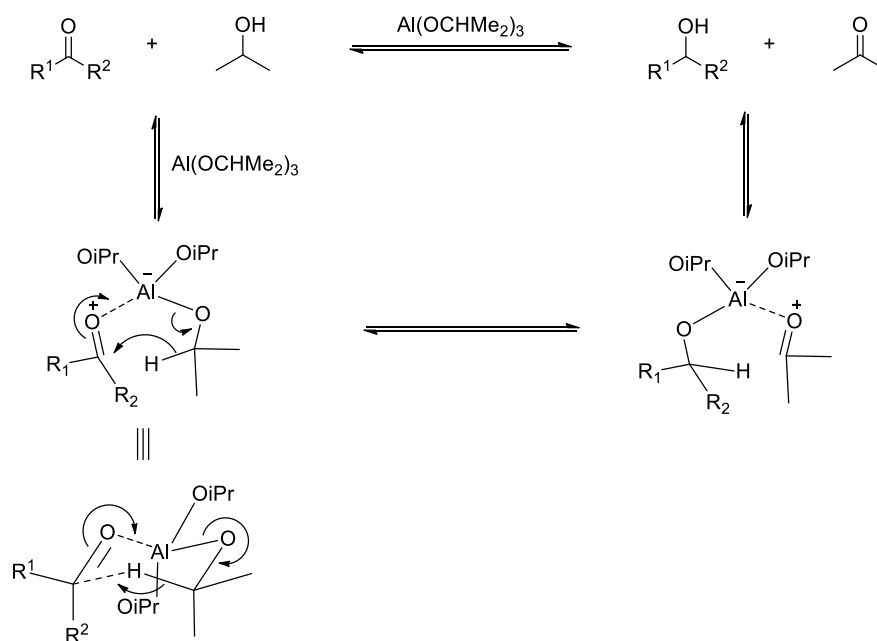
e) How to explain the following observations:



Solution

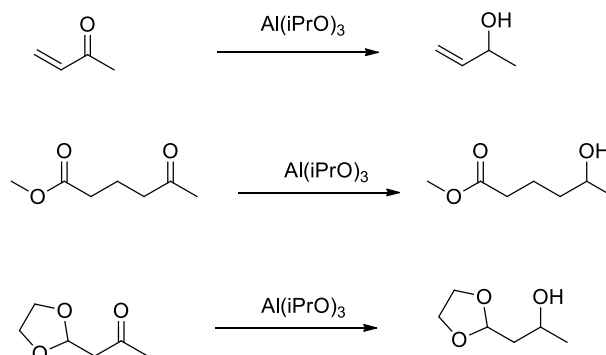
a) Oppenauer oxidation

b) Mechanism of MPV or Oppenauer oxidation

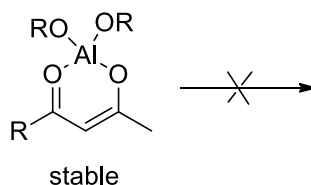


c) By removing volatile acetone or by using an excess of isopropanol (Le Chatelier's principle)

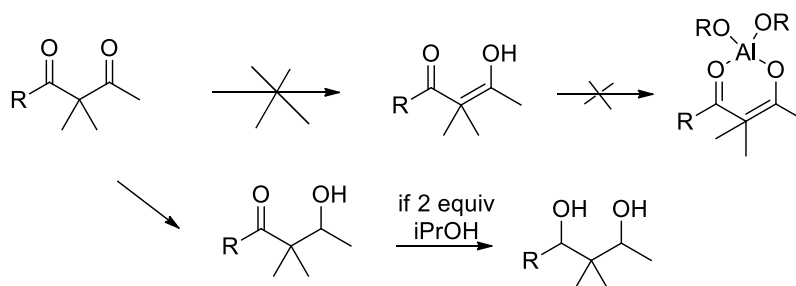
d)



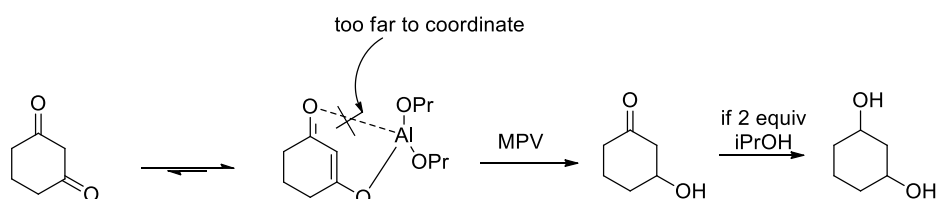
e) **1.** β -Diketones can form stable β -enolates which coordinate strongly with $\text{Al}(\text{OR})_3$ preventing the MPV transformation:



2. Dialkylated β -Diketones cannot form β -enolates as in the previous example because there is no enolizable proton. So the reaction proceeds:

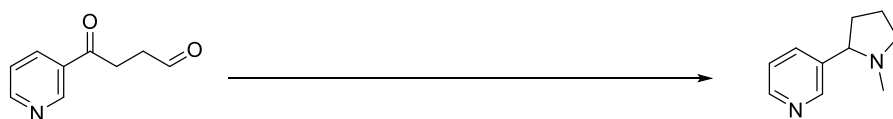
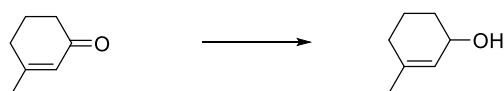
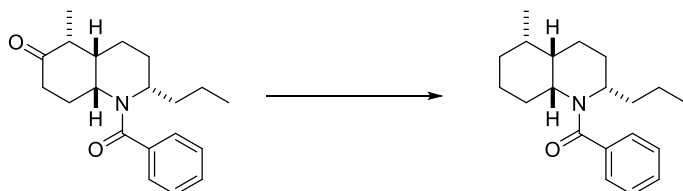
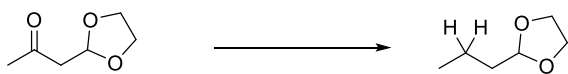


3. $\text{Al}(\text{OR})_3$ cannot coordinate strongly with cyclic β -diketones as in the first example. So the reaction proceeds:

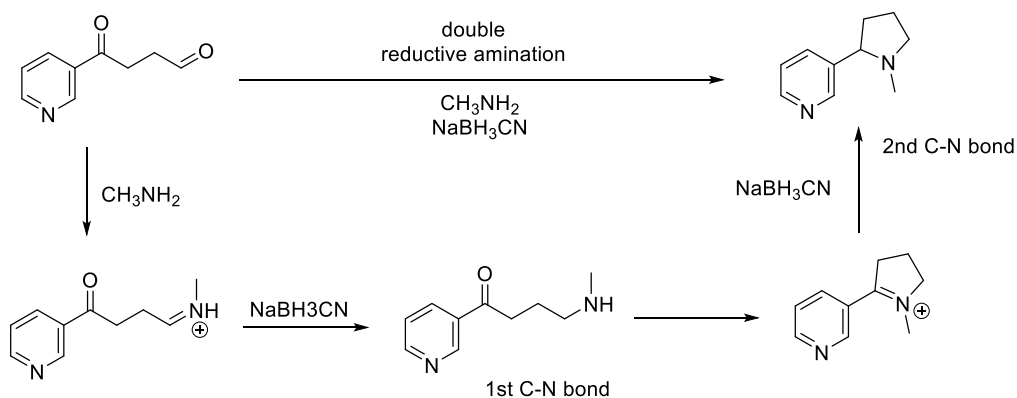
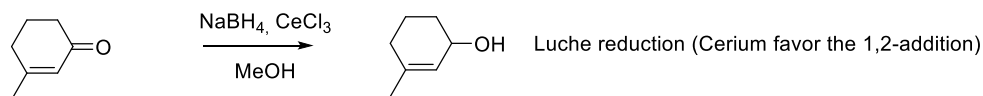
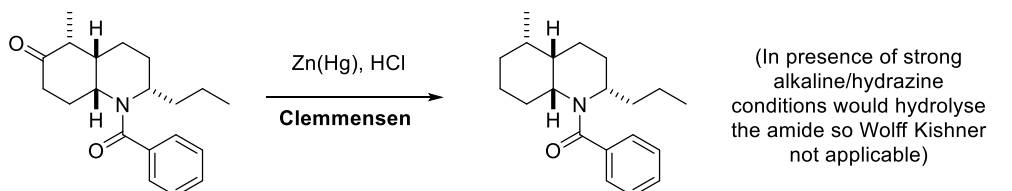
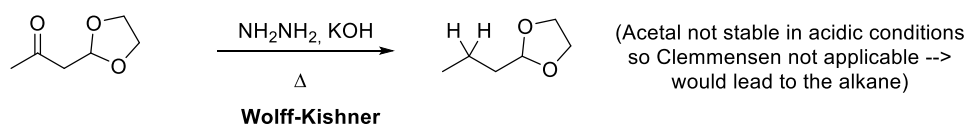


Problem 3

Suggest transformation(s) that would be suitable for each of the following selective or partial reduction.



Solution



REMINDER: Activity of carbonyl compounds to nucleophiles

The activity of carbonyl compounds toward nucleophiles is dependent on positive charge on carbon atom. The more positive charge it carries, the more active it is. Consequently, the group which decreases electron density or increases positive charge on carbon atom will increase its activity and so on.

decrease
of activity

↓

	X	Effect	Activity
	Cl, Br (acyl halide)	-I	strongly increase
	OCOR (anhydride)	-I	increase
	H (aldehyde)	none	none
	Alkyl (ketone)	+I	slightly decrease
	OAlkyl (ester)	-I, +C (-I << +C)	decrease
	NHAlkyl (amide)	-I, +C (-I << +C)	decrease
	O- (carboxylate)	-I, +C (-I << +C)	strongly decrease

Notes:

I : inductive effect

C: conjugative effect

- : withdrawing electron

+: donating electron