Addition Of Grignard Reagents To Aldehydes And Ketones

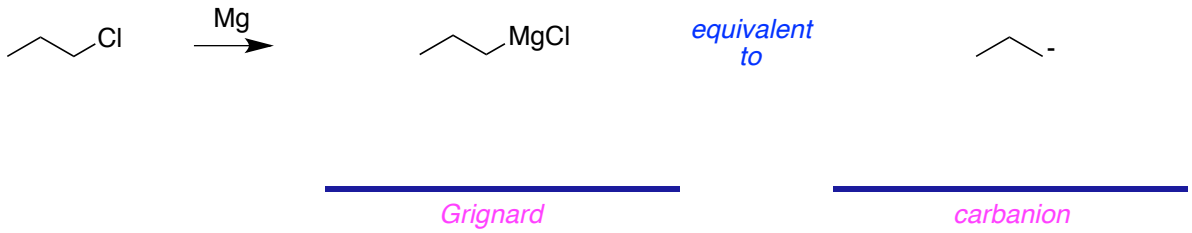
from chapter(s) _____ in the recommended text

A. Introduction

.

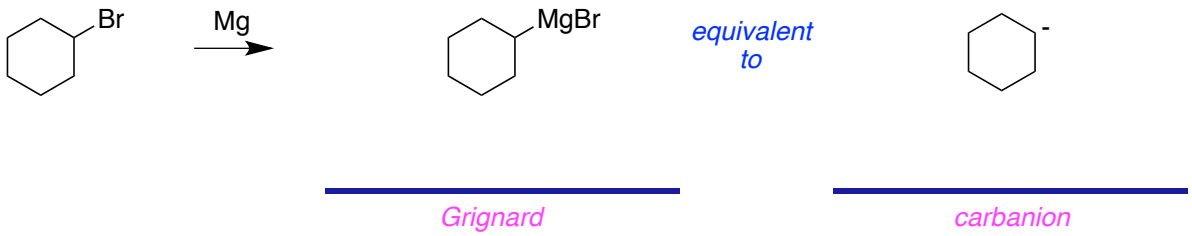
B. Grignard Reagents: A Type Of Carbanion Equivalents

magnesium;
strong base
cannot be formed from compounds liberating *ethene*.



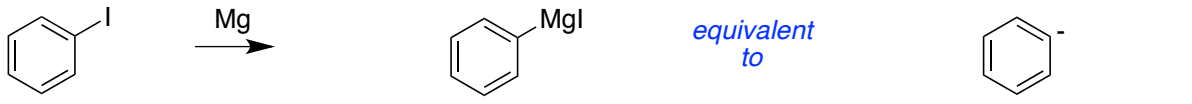
Grignard *carbanion*

hydrocarbon



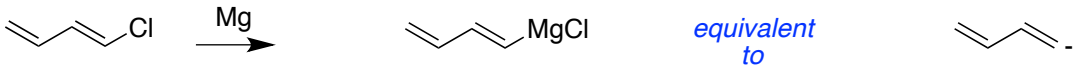
Grignard *carbanion*

hydrocarbon



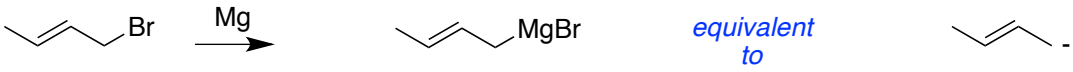
Grignard carbanion

hydrocarbon



Grignard carbanion

hydrocarbon



Grignard *carbanion*

hydrocarbon

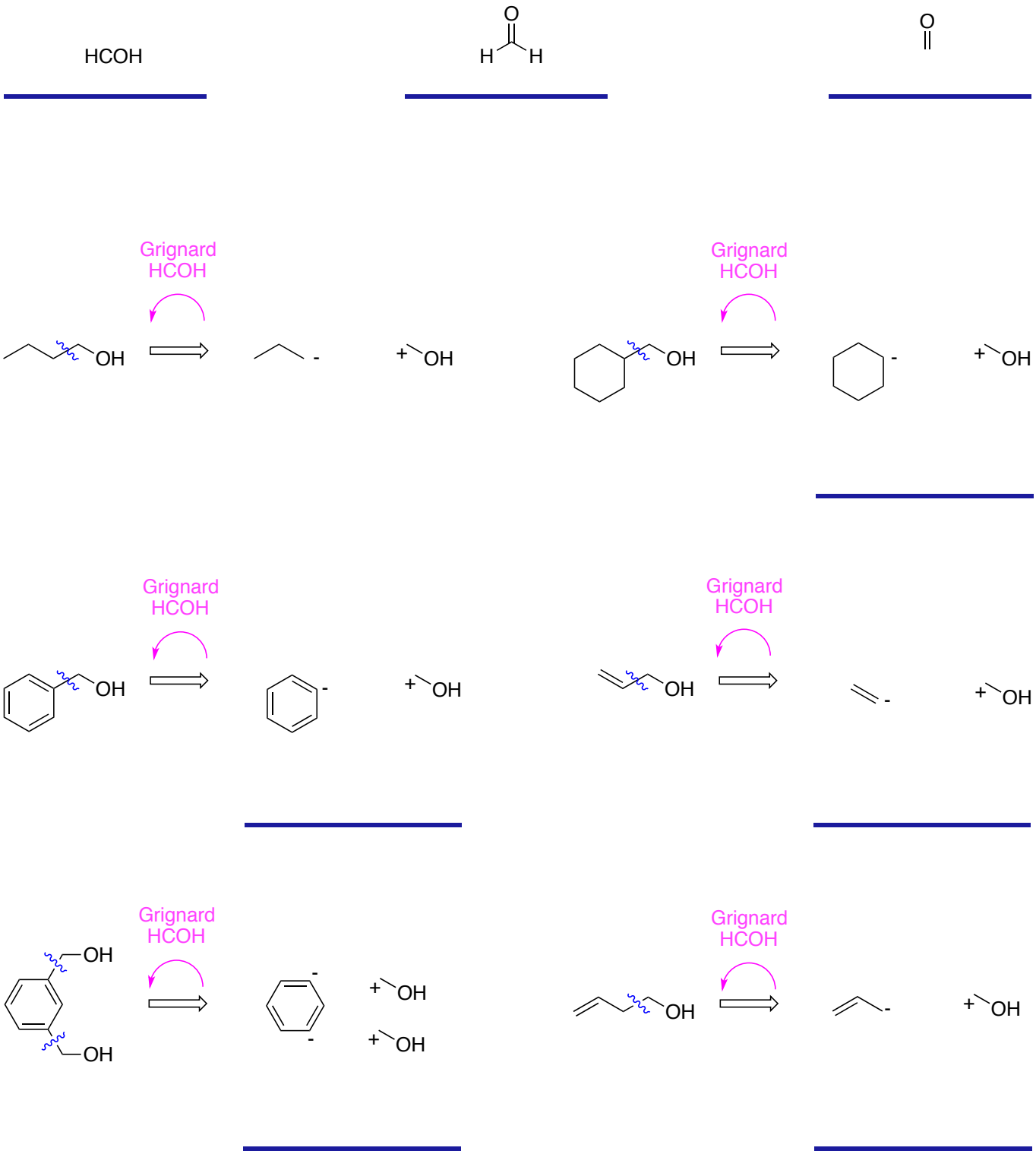
1,2-dichloroethane bromobenzene benzyl bromide butane

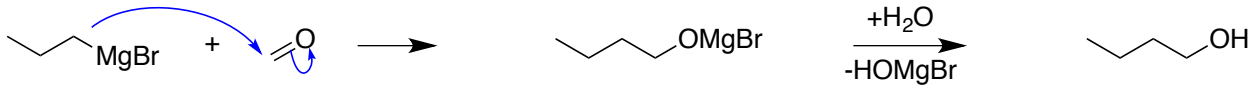
allyl chloride 2-chloropropane 1,2-diiodopropane 2-chloroethanol

diethyl ether fluoroethane bromoethanal 3-iodopropanol

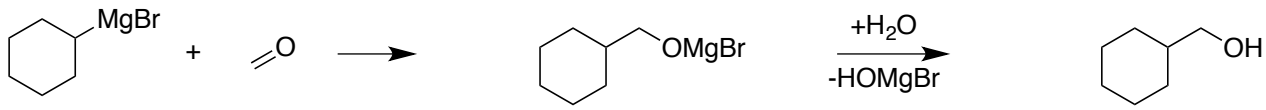
chloro(methoxy)methane 1-bromo-3-methoxy-ethanal bromoethane

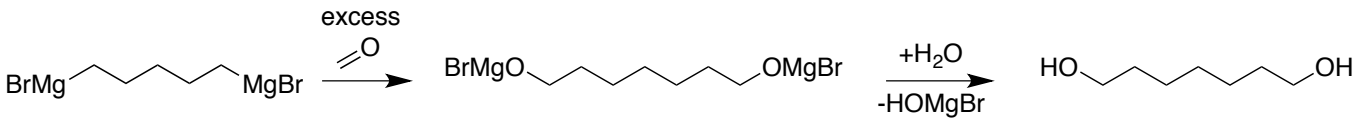
C. Reactions Of Methanal With Grignard Reagents

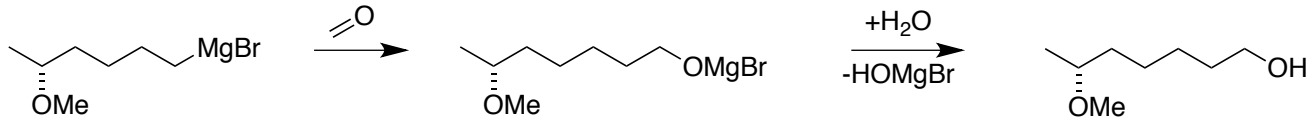


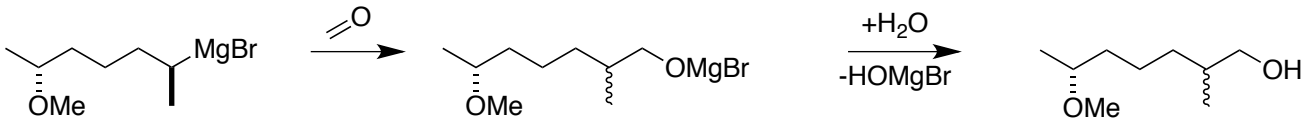


primary alcohols
one more

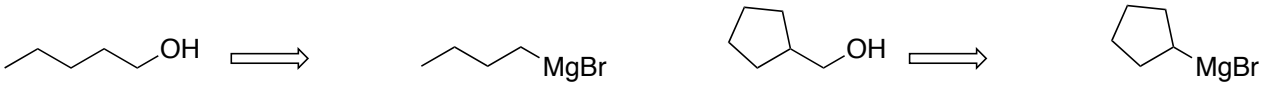




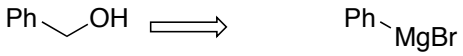


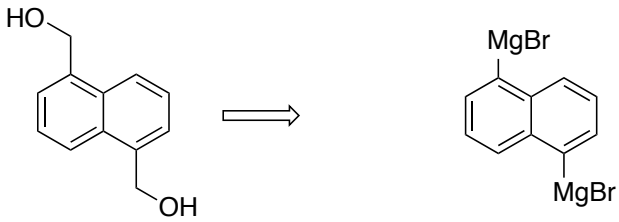


primary

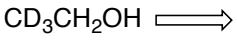


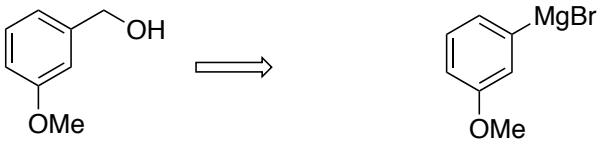
a di-Grignard

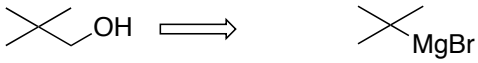


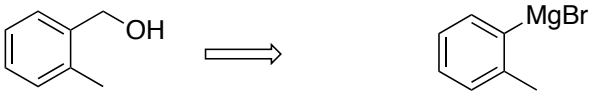


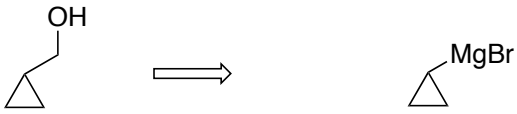
a di-Grignard





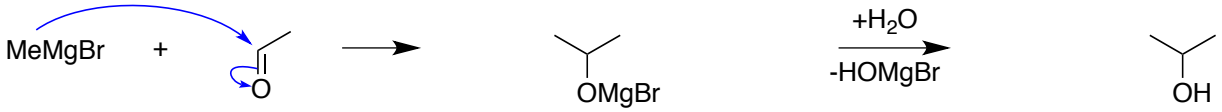




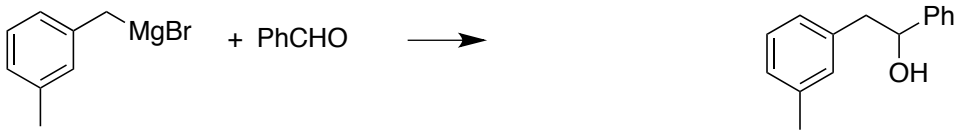


more basic than
compounds *irreversibly*.
primary because methanal has *two*
secondary alcohols.
is unique

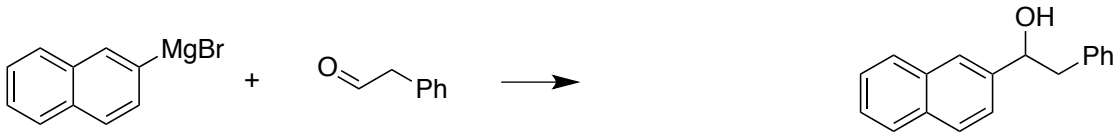
D. Reactions Of Other Aldehydes With Grignards



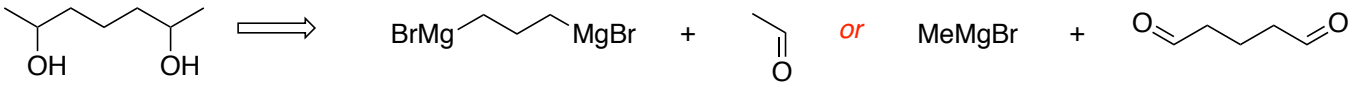
give *secondary* alcohols with *the same*

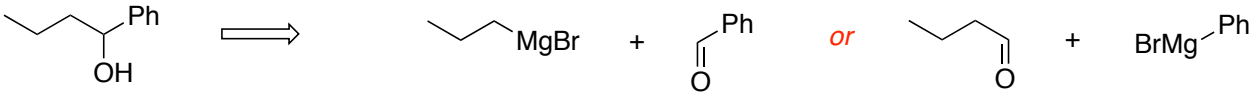


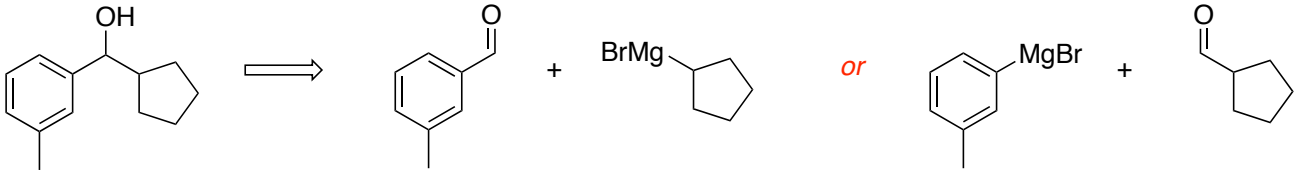
Grignard reagents are *more* basic than nucleophiles like methoxide, and add to carbonyl compounds *irreversibly*.
The alcohols from reactions of Grignards with methanal are *primary* because methanal has *two* hydrogens attached to the carbonyl group.
Reactions of Grignards with other aldehydes must give *secondary* alcohols; methanal *is* unique.

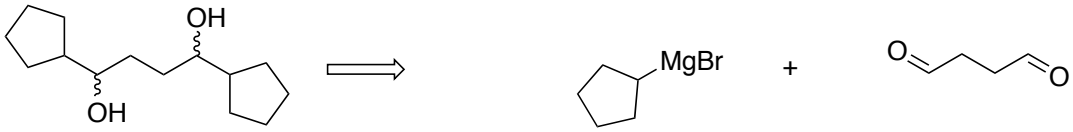


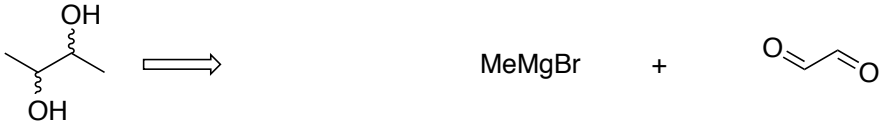
secondary alcohols


OH
OH
BrMg
MgBr
+
O
or
MeMgBr
+
O
O

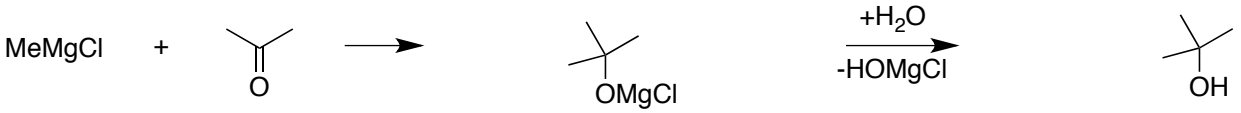

Ph
OH
MgBr
+
Ph
O
or
O
+
BrMg
Ph


OH
O
+
BrMg
or
MgBr
+
O

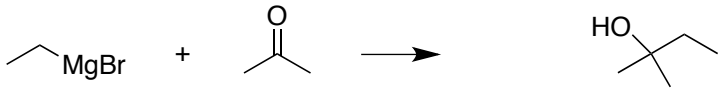

OH
OH
MgBr
+
O
O

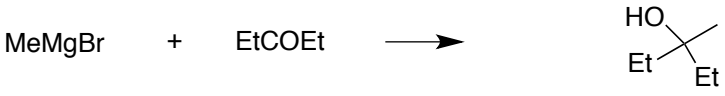

OH
OH
MeMgBr
+
O
O

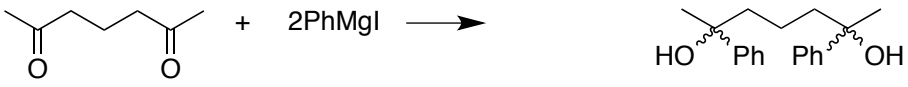
E. Reactions Of Ketones With Grignards

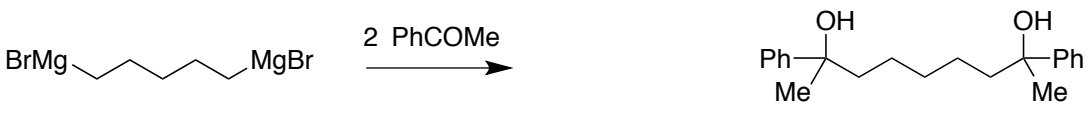


tertiary alcohols.
the same
must be the

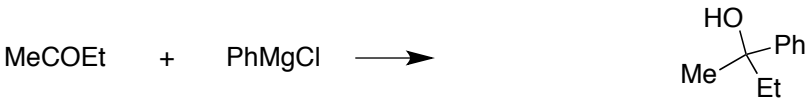


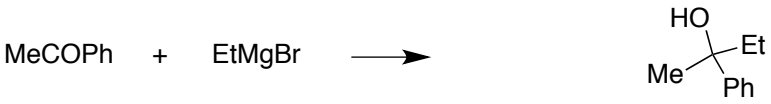


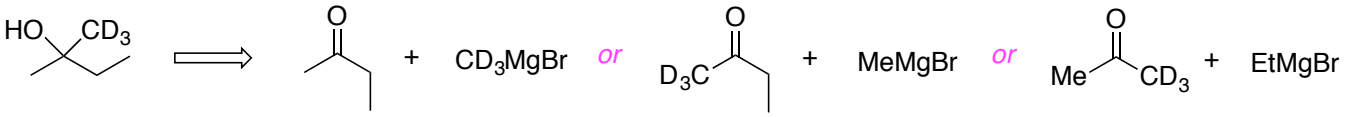



BrMg
MgBr
2 PhCOMe
OH
OH
Ph
Ph
Me
Me

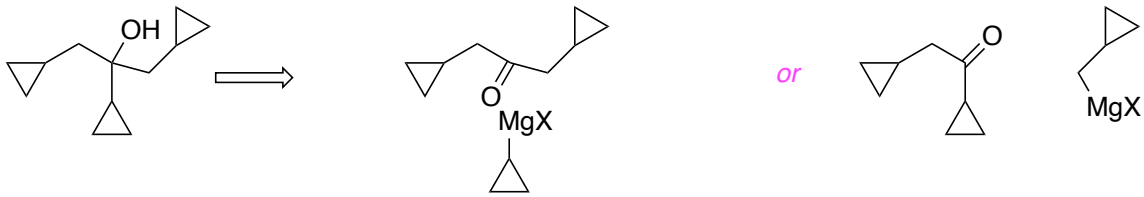

O
MgBr
OH

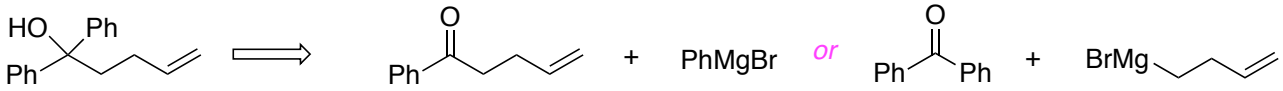

MeCOEt
+
PhMgCl
HO
Ph
Me
Et

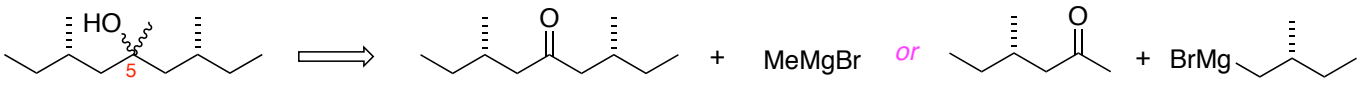

MeCOPh
+
EtMgBr
HO
Et
Me
Ph



THIS PROBLEM HAS BEEN CHANGED FOR THE SECOND EDITION OF THE BOOK

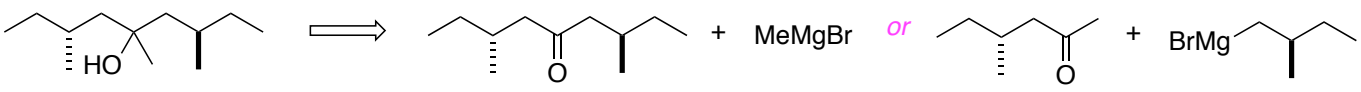






is

is not possible

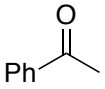


F. Complimentary Grignard and Hydride Reductions

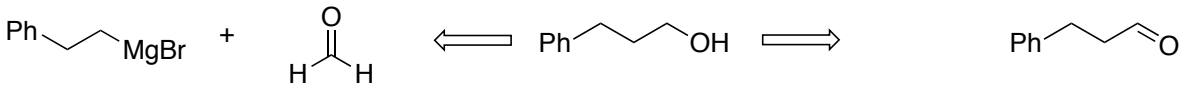
a Grignard route

+ MeMgBr + PhMgBr

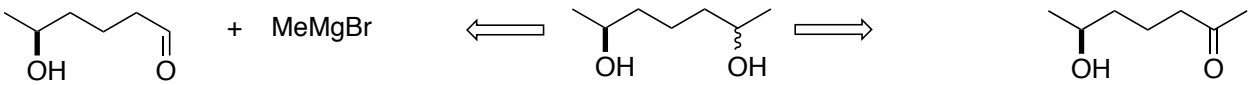
hydride route



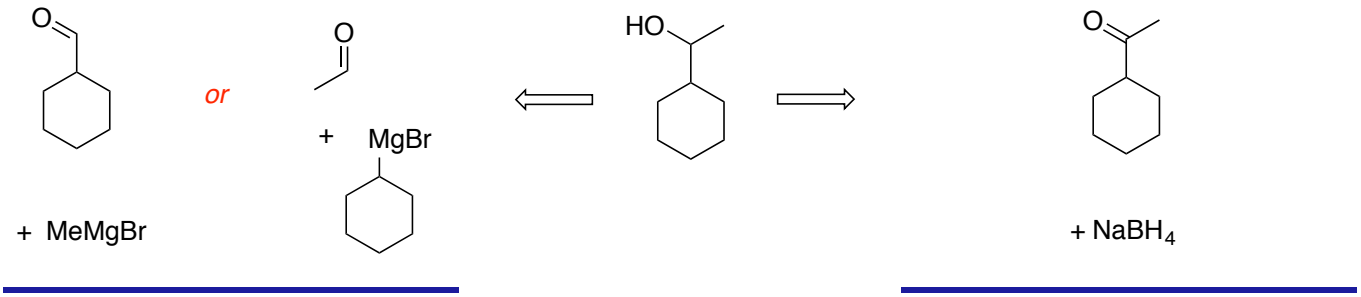
+ $NaBH_4$

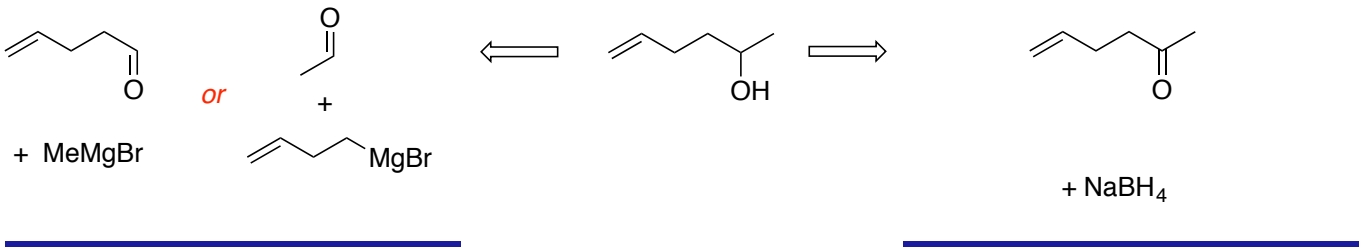


+ $NaBH_4$

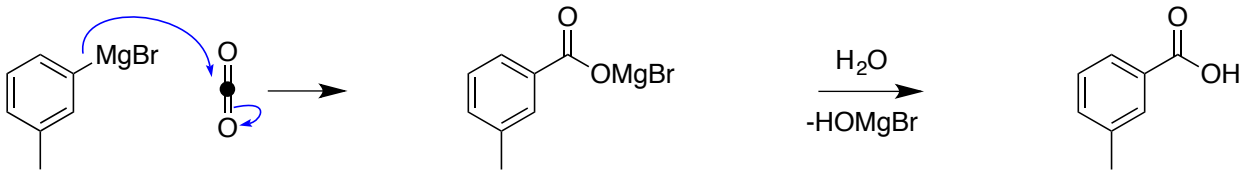


+ $NaBH_4$

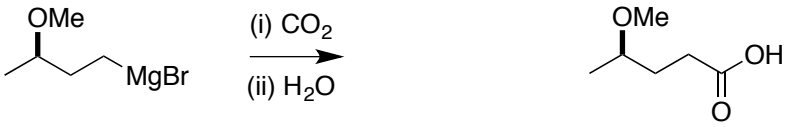

O
or
O
+ MgBr
HO
O
+ MeMgBr
+ NaBH4


O
O
or
+
OH
O
+ MeMgBr
MgBr
+ NaBH4

G. Reactions Of Carbon Dioxide With Grignards

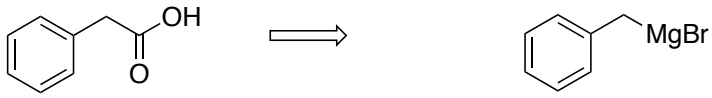


carboxylic acid.
one more carbon than the Grignard.




MgBr
(i) CO_2
(ii) H_2O
COOH


MgBr
BrMg
(i) CO_2
(ii) H_2O
COOH
HOOC



almost always