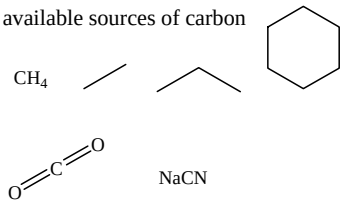
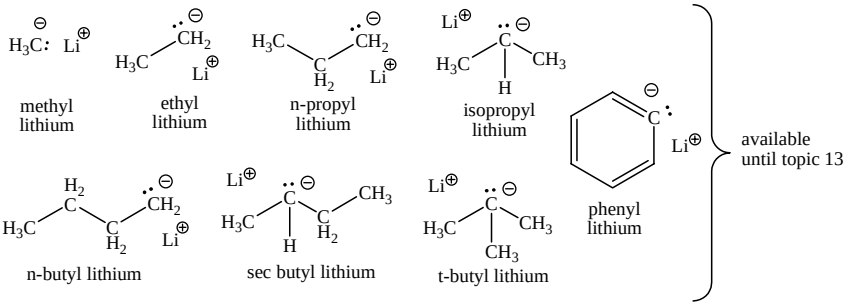
Chem 315/316 Reactions Name _____

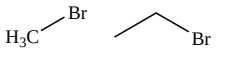
available sources of carbon



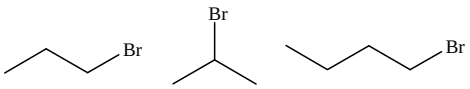


Bromo organic compounds

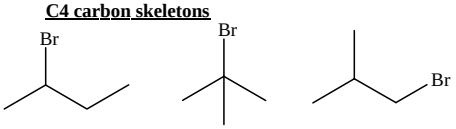
C1 & C2 carbon skeletons



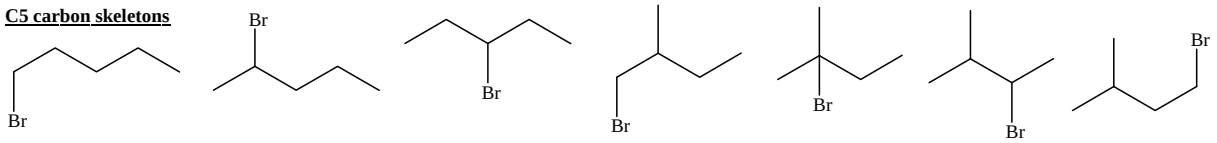
C3 carbon skeletons



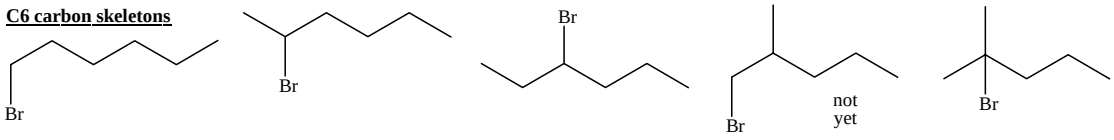
C4 carbon skeletons

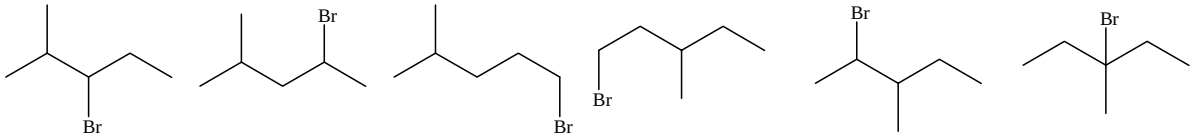


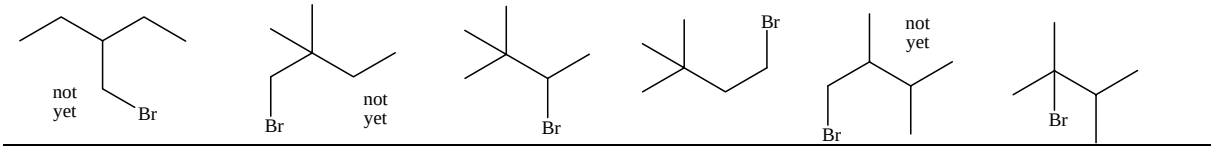
C5 carbon skeletons



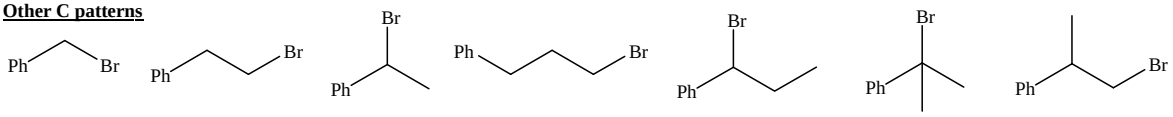
C6 carbon skeletons

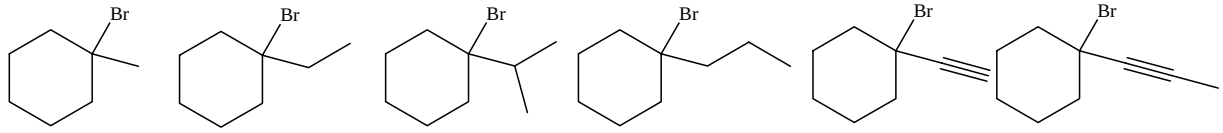




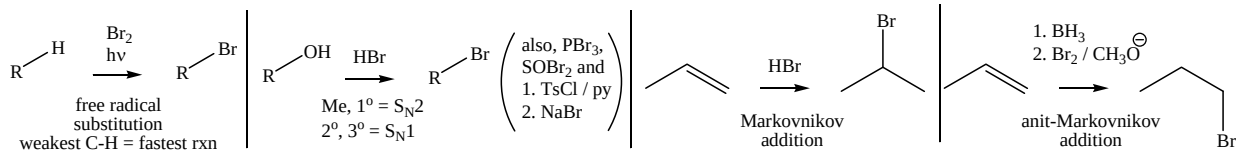


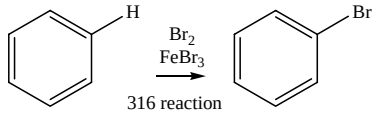
Other C patterns





A few ways to make R-Br (generic and specific)

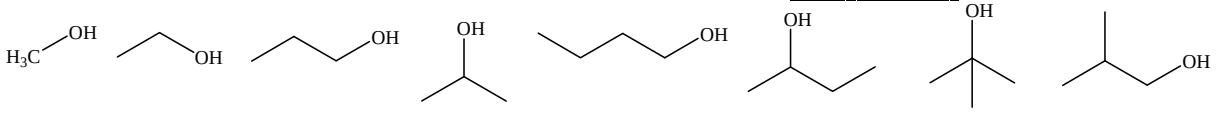




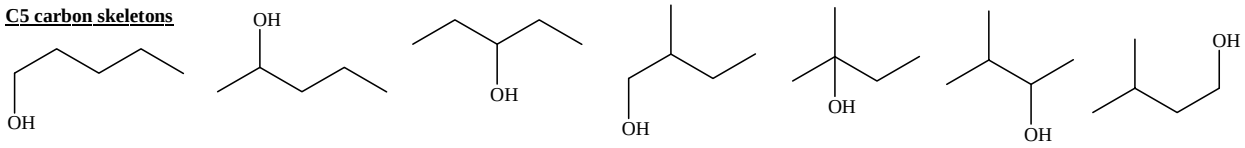
Rearrangements are possible with R^+ intermediates.

Alcohols

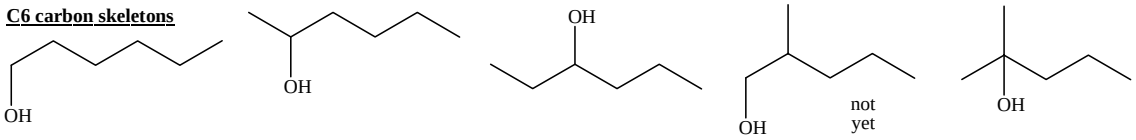
C1 & C2 carbon skeletons **C3 carbon skeletons** **C4 carbon skeletons**

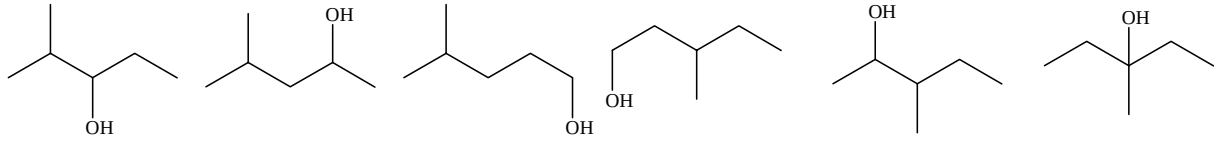


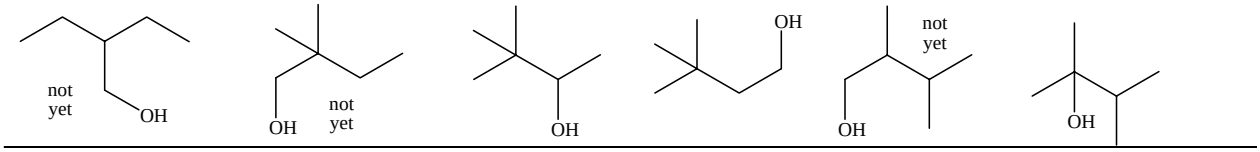
C5 carbon skeletons



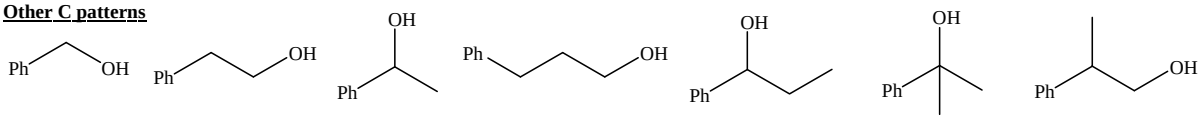
C6 carbon skeletons

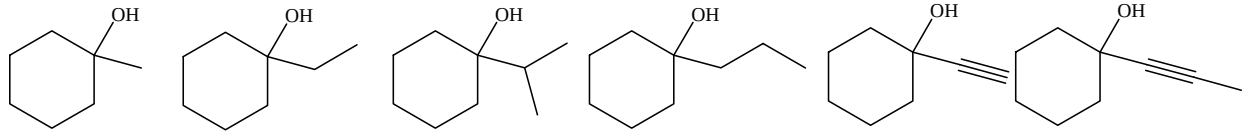




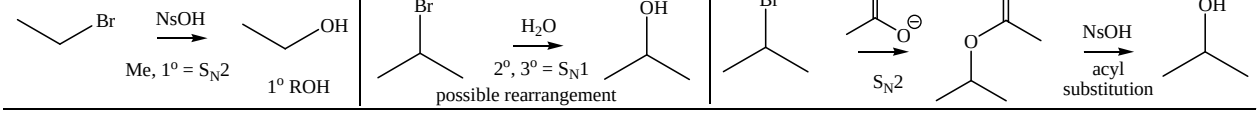


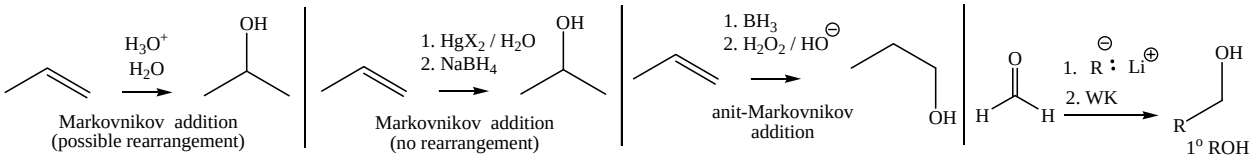
Other C patterns

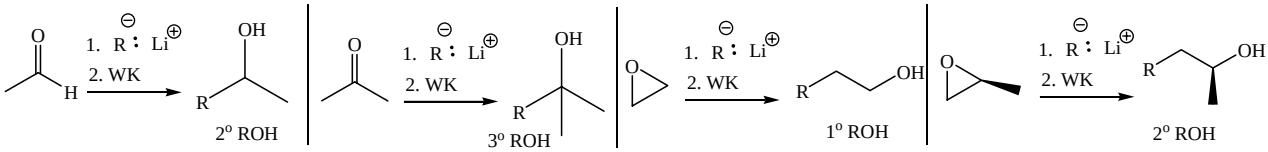


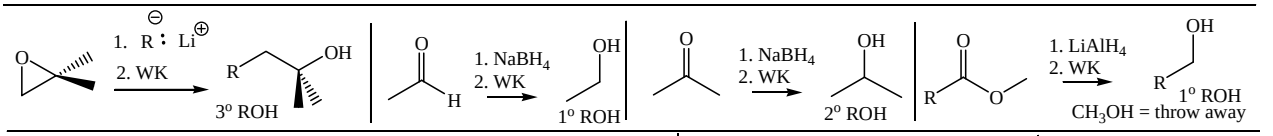


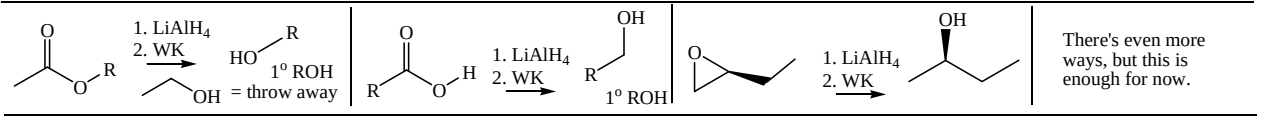
A few ways to make R-OH







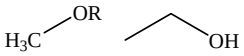




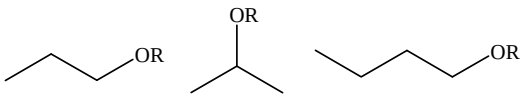
Rearrangements are possible with R^+ intermediates.

Ethers

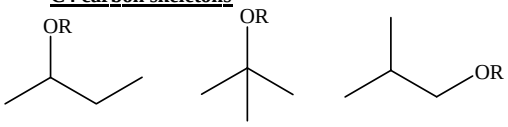
C1 & C2 carbon skeletons



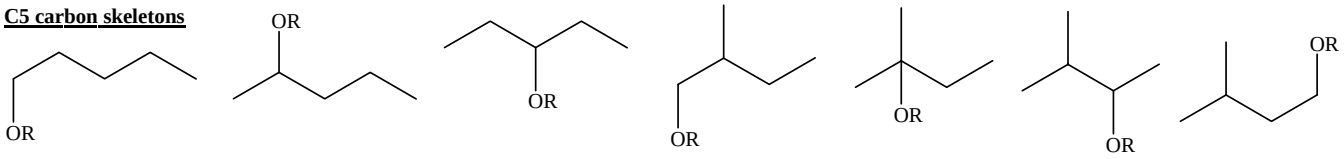
C3 carbon skeletons



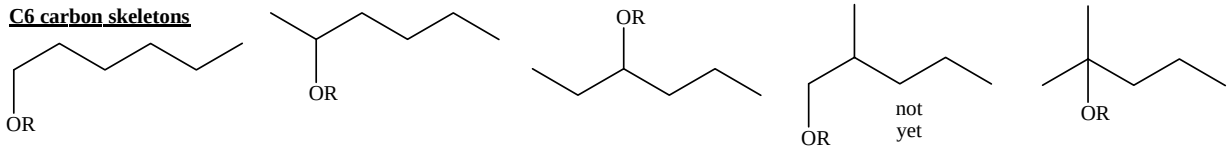
C4 carbon skeletons

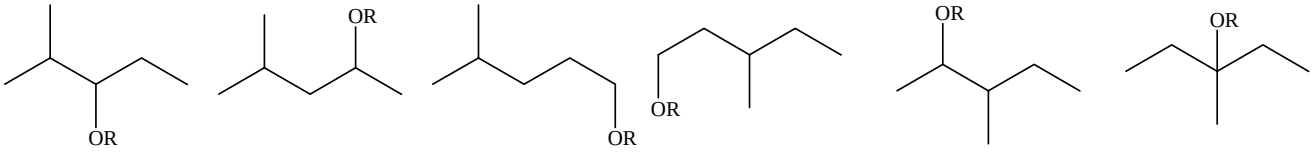


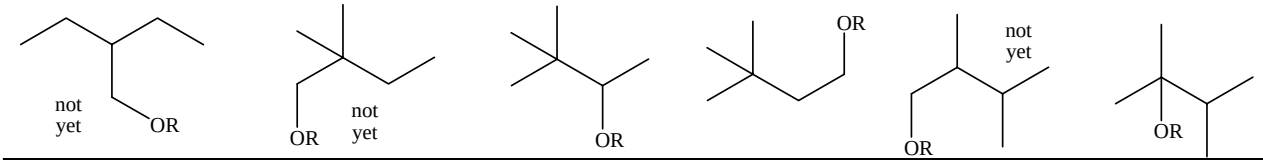
C5 carbon skeletons



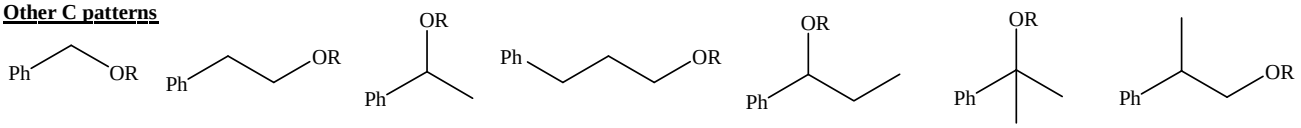
C6 carbon skeletons



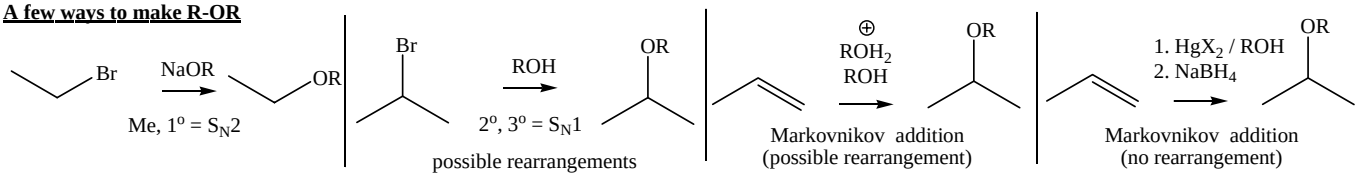




Other C patterns



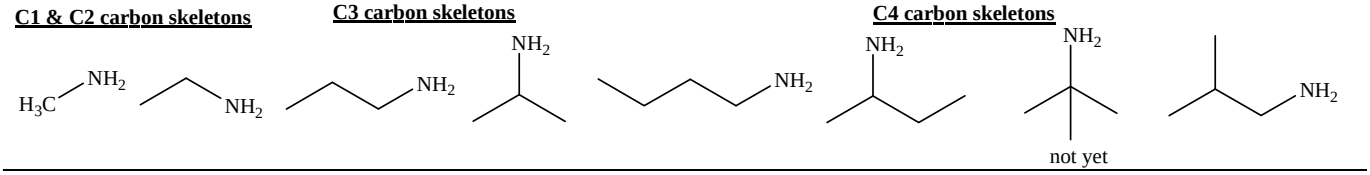
A few ways to make R-OR



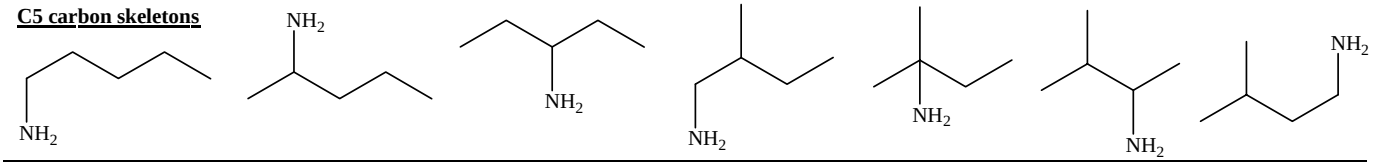
R = a second carbon pattern

Amines

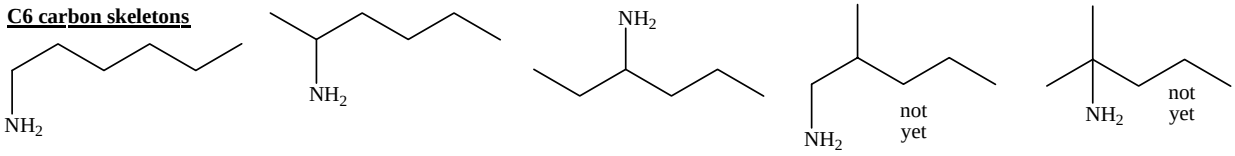
C1 & C2 carbon skeletons **C3 carbon skeletons** **C4 carbon skeletons**

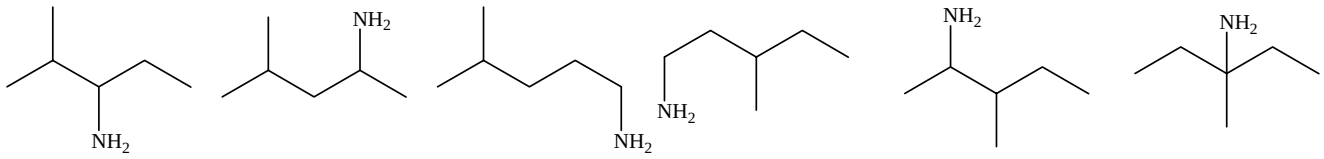


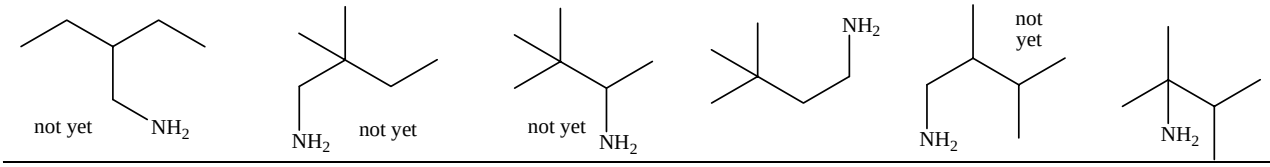
C5 carbon skeletons



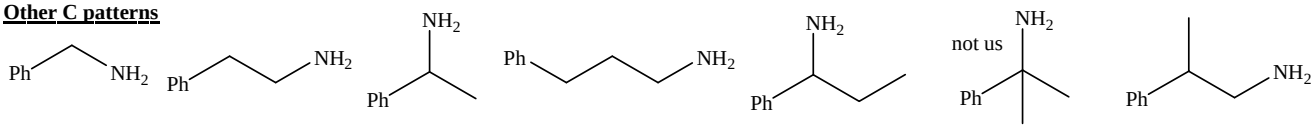
C6 carbon skeletons



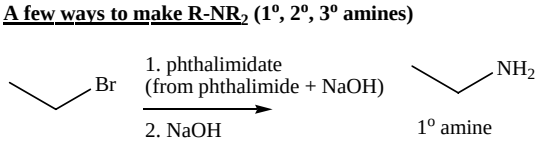


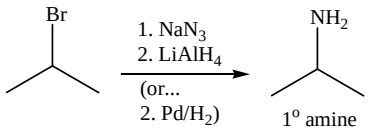


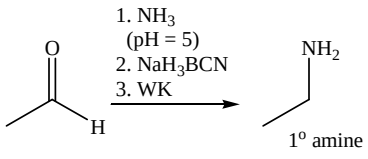
Other C patterns

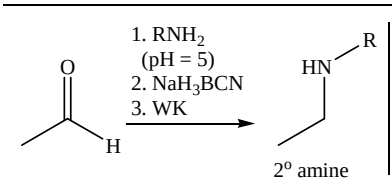


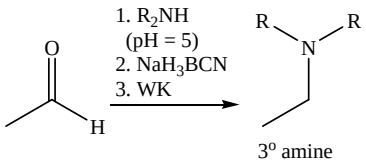
A few ways to make R-NR_2 (1^o, 2^o, 3^o amines)

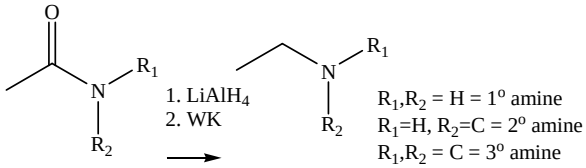


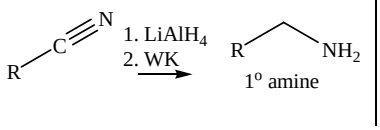






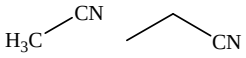




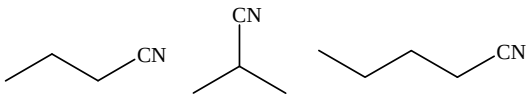


Nitriles

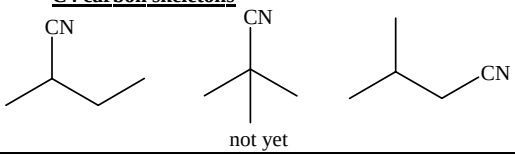
C1 & C2 carbon skeletons



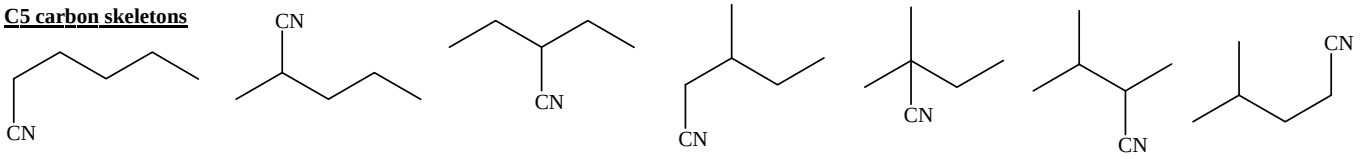
C3 carbon skeletons



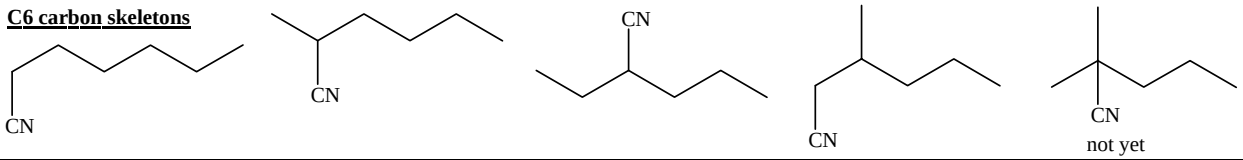
C4 carbon skeletons

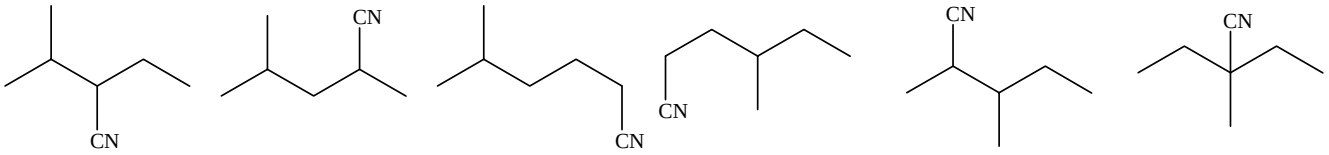


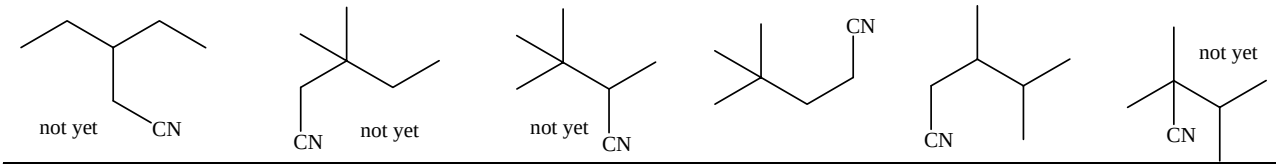
C5 carbon skeletons



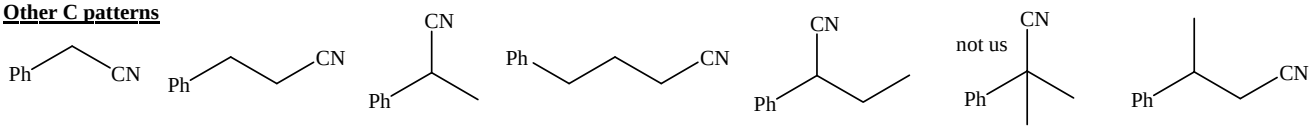
C6 carbon skeletons



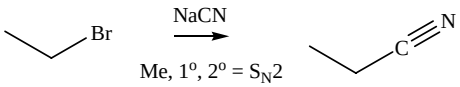


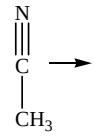


Other C patterns

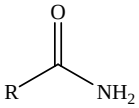


A way to make R-CN

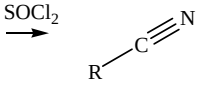




1° amine (a. $LiAlH_4$ b. WK)
1° amide (HCl/H_2O)
acid ($H_2SO_4/H_2O/\Delta$)
aldehyde (a. DIBAH b. WK)
ketone (a. RMgBr b. WK)

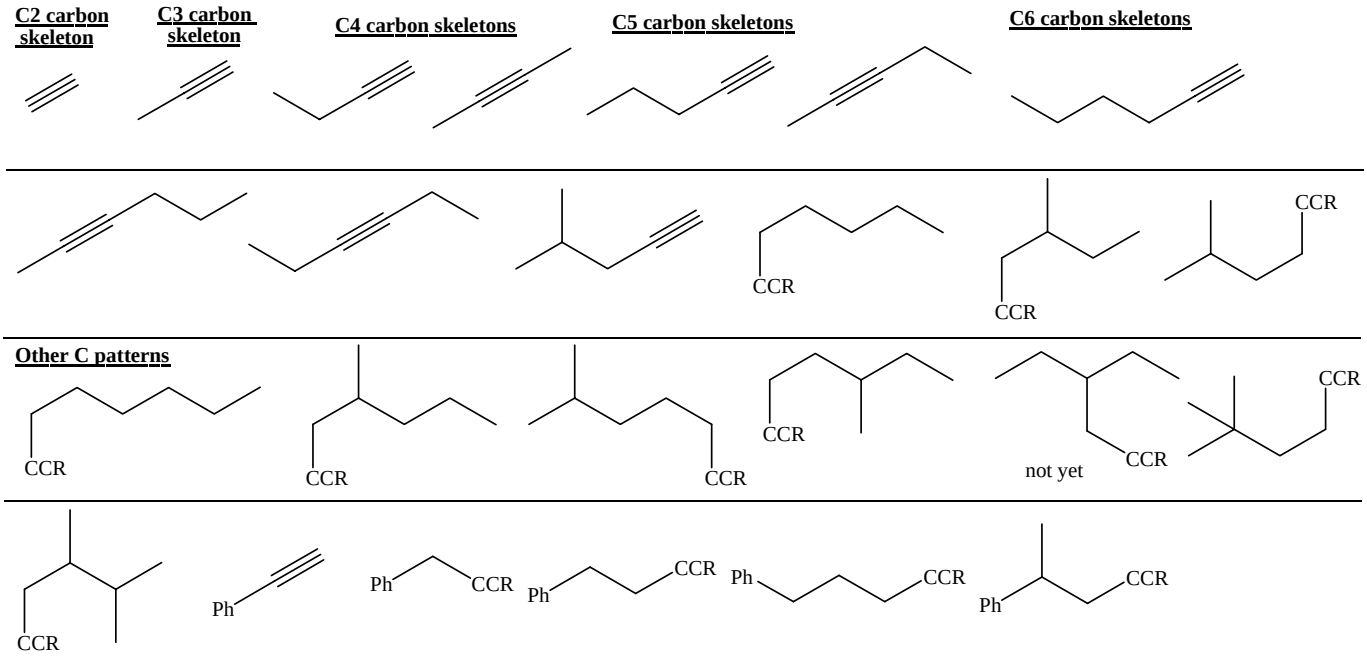


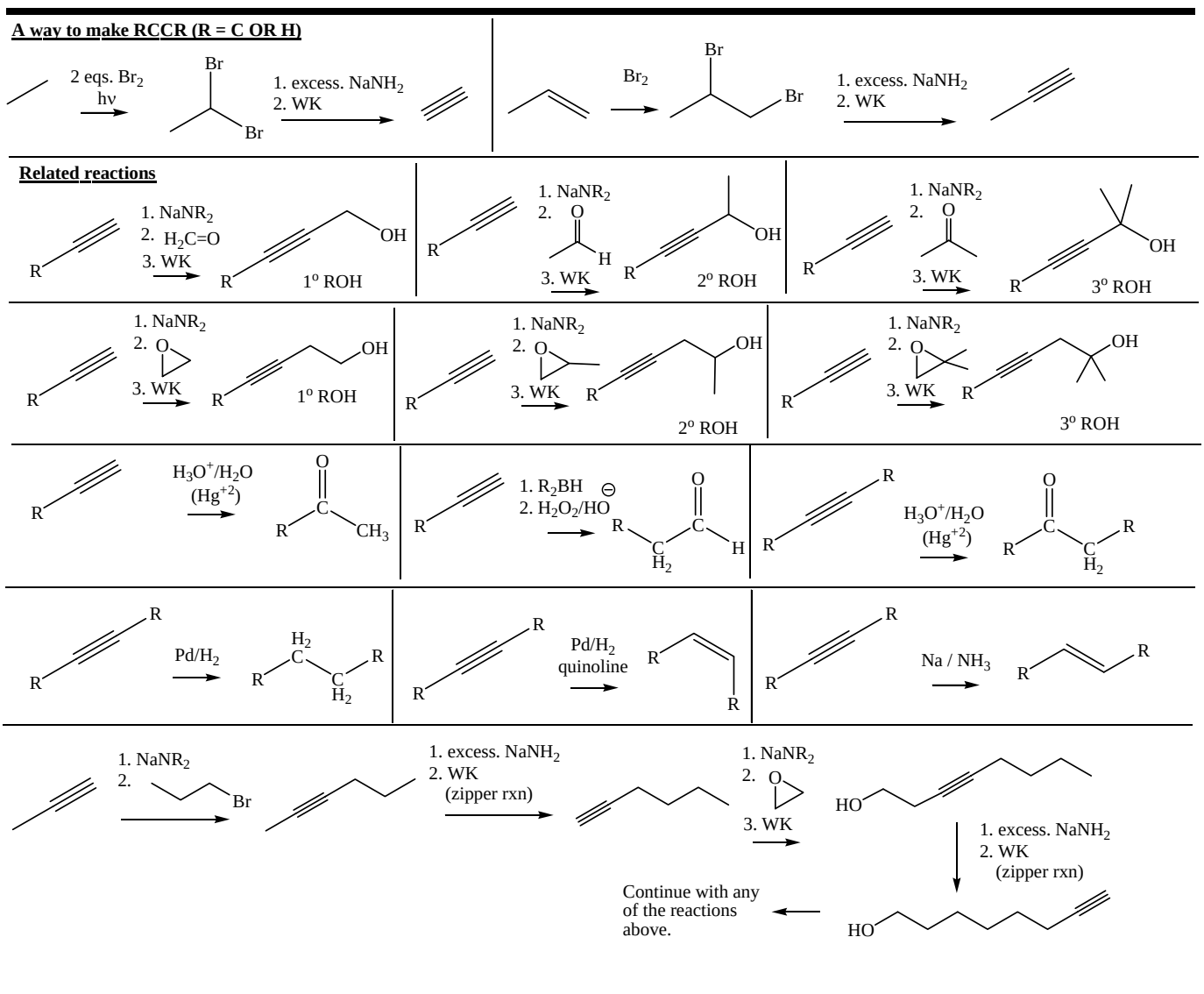
1° amides



good mechanism problem

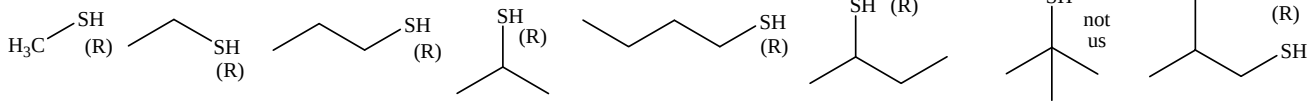
Alkynes


C2 carbon skeleton
C3 carbon skeleton
C4 carbon skeletons
C5 carbon skeletons
C6 carbon skeletons
CCR
Other C patterns
not yet
Ph

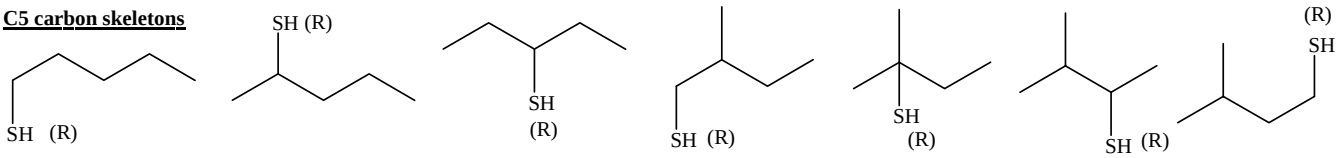

A way to make RCCR (R = C OR H)
2 eqs. Br2
hν
1. excess. NaNH2
2. WK
Br2
Related reactions
1. NaNR2
2. H2C=O
3. WK
1º ROH
2º ROH
3º ROH
H3O+/H2O
(Hg+2)
1. R2BH
2. H2O2/HO
Pd/H2
quinoline
Na / NH3
(zipper rxn)
Continue with any of the reactions above.

Thiols and Sulfides

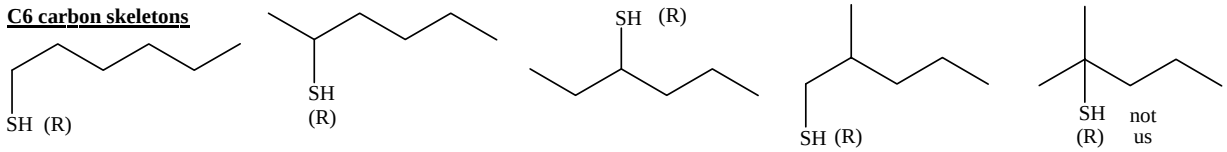
C1 & C2 carbon skeletons **C3 carbon skeletons** **C4 carbon skeletons**

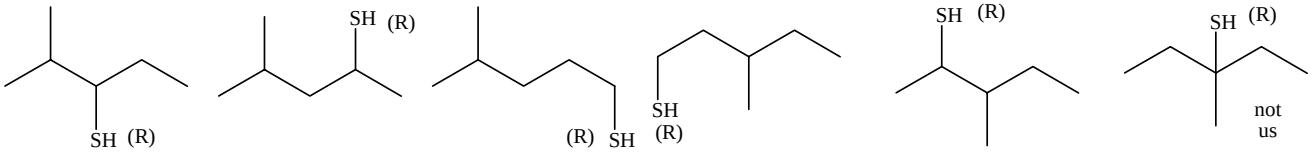


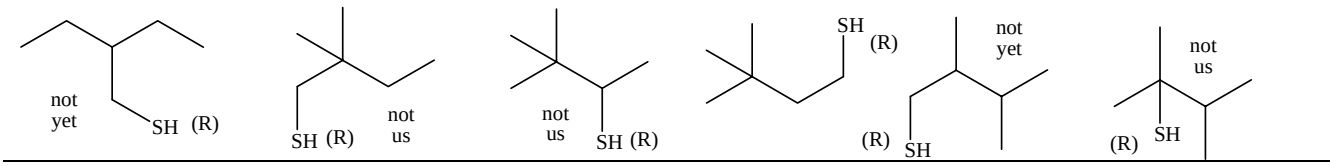
C5 carbon skeletons



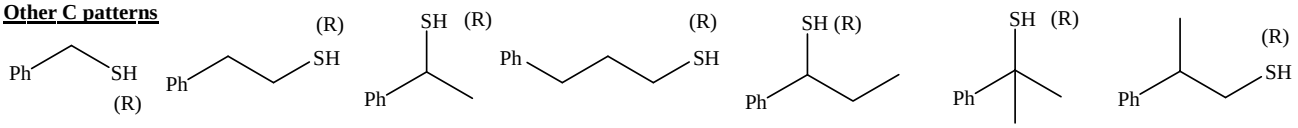
C6 carbon skeletons

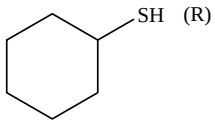




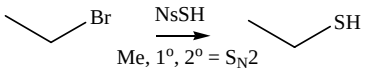


Other C patterns

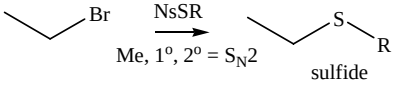




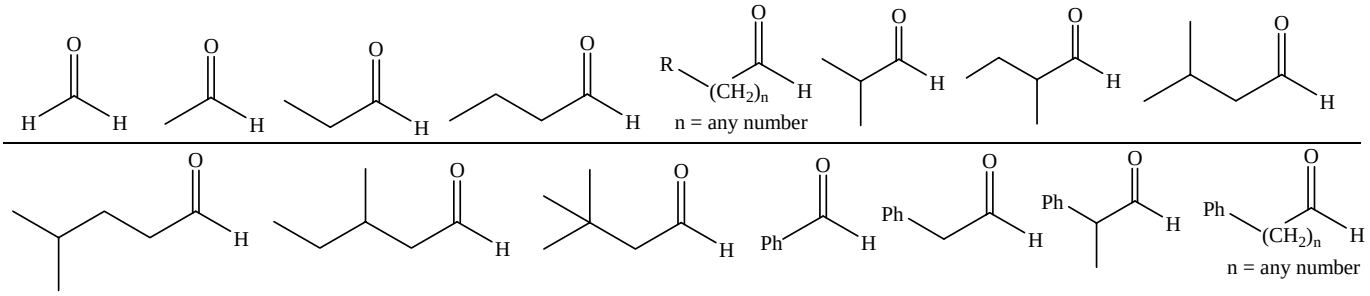
A way to make R-SH



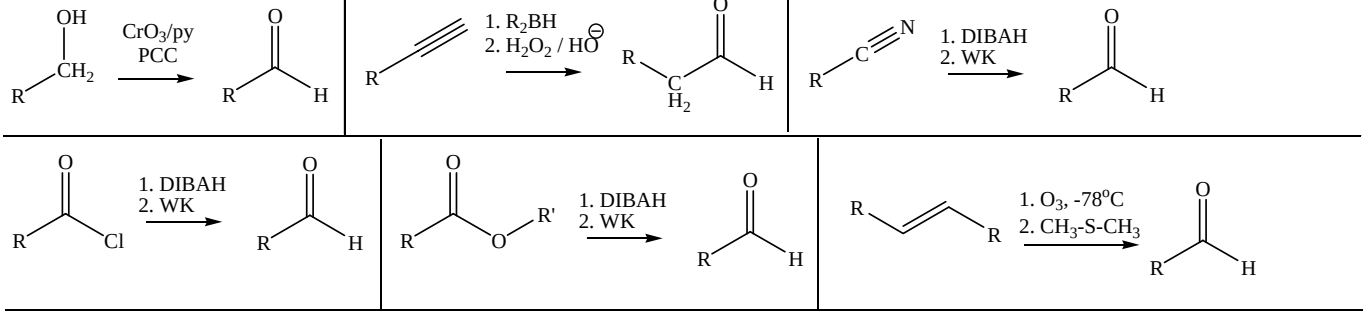
A way to make R-S-R



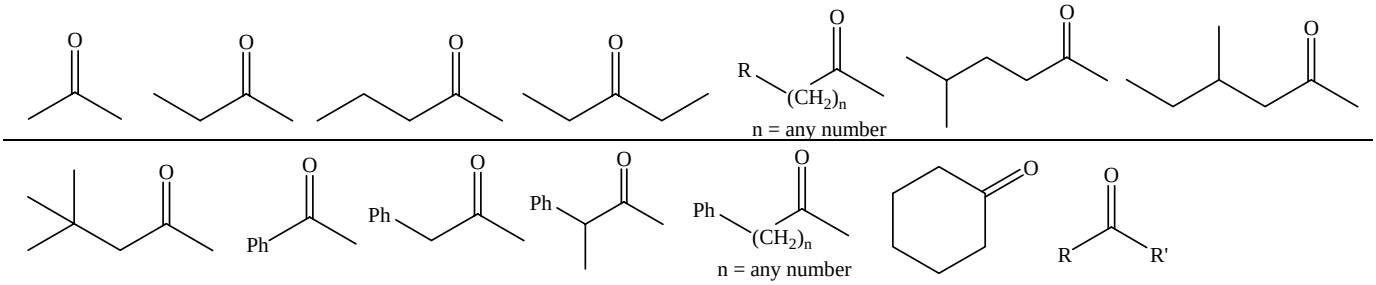
Aldehydes



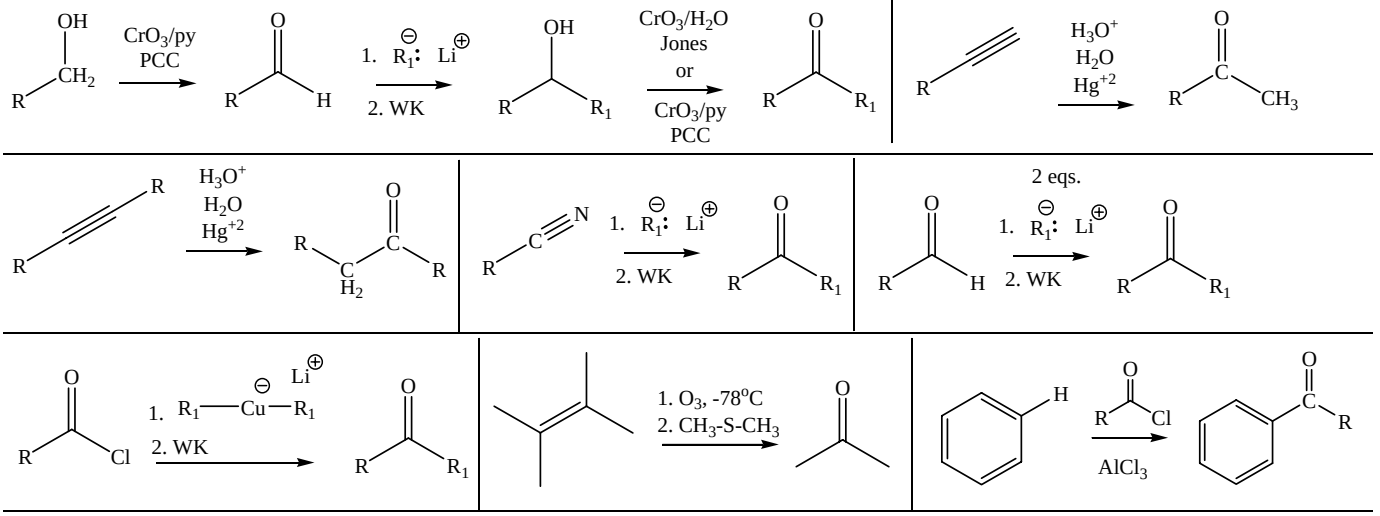
A few ways to make RCHO



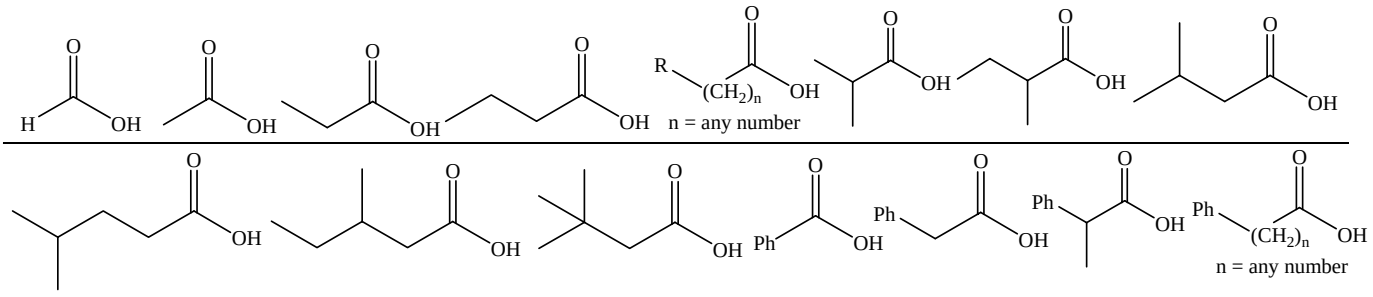
Ketones



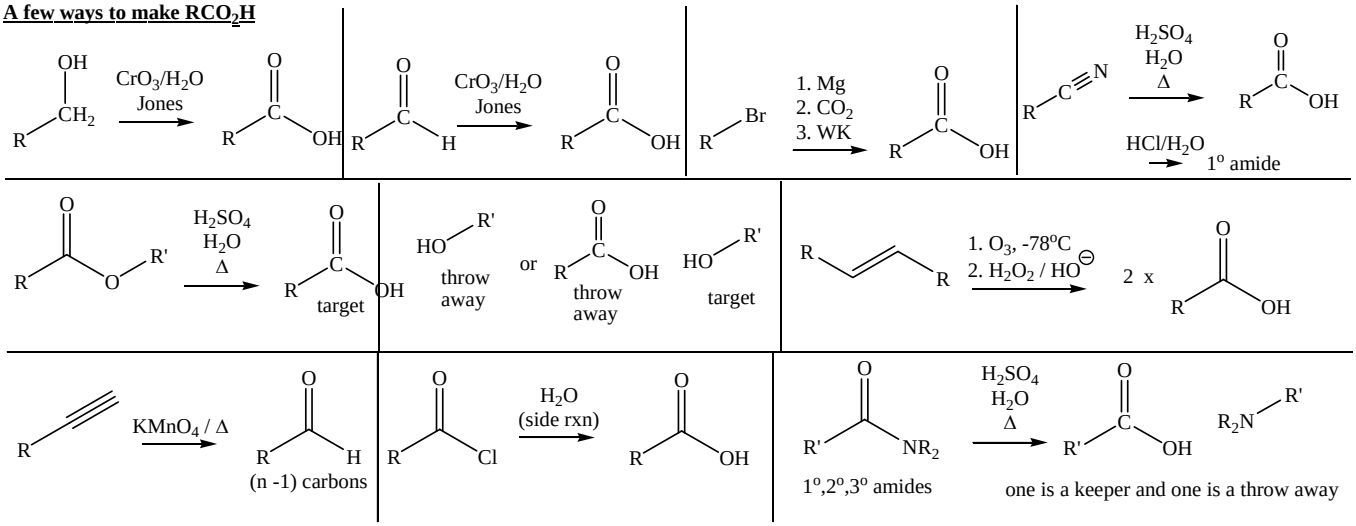
A few ways to make RCOR'



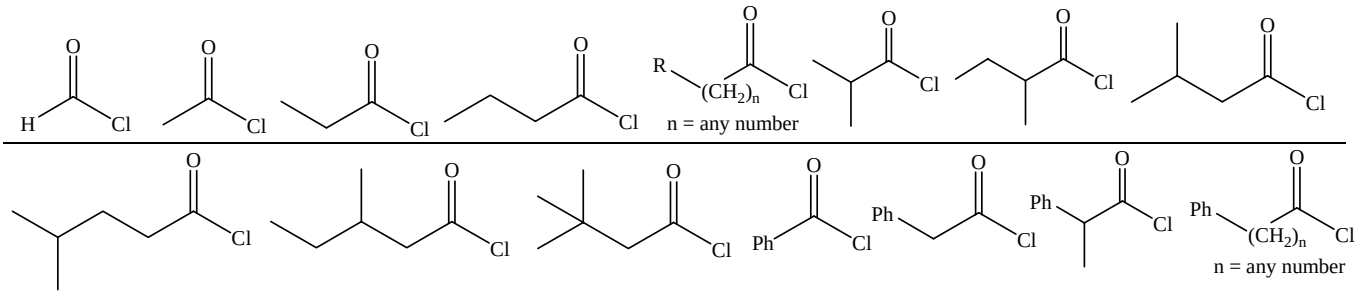
Carboxylic acids



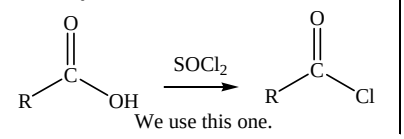
A few ways to make RCO_2H

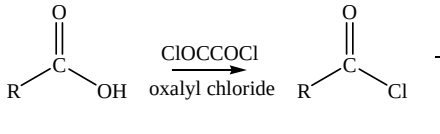


Acid chlorides



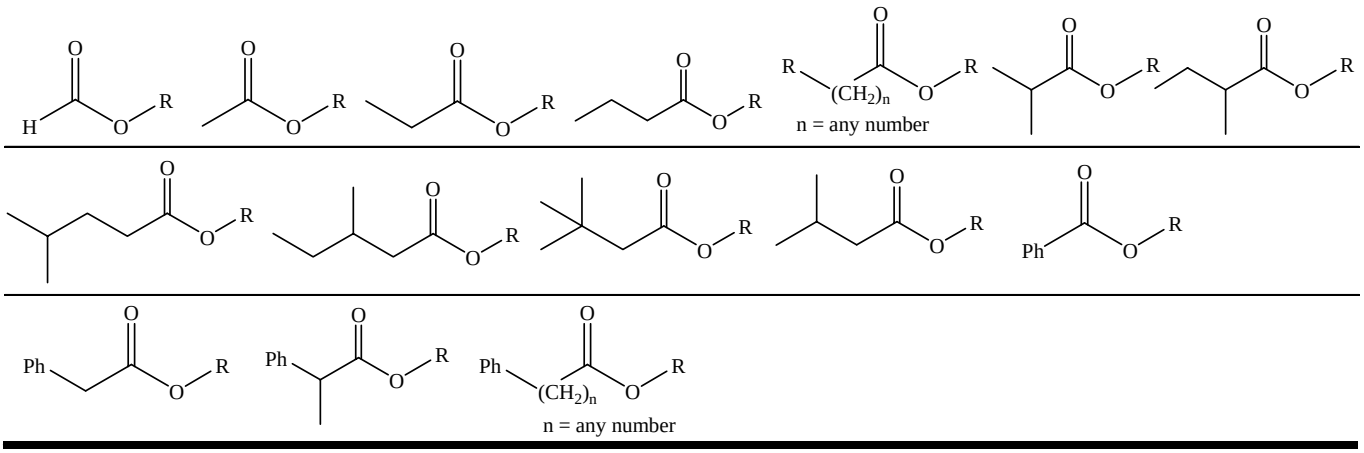
A few ways to make RCOCl



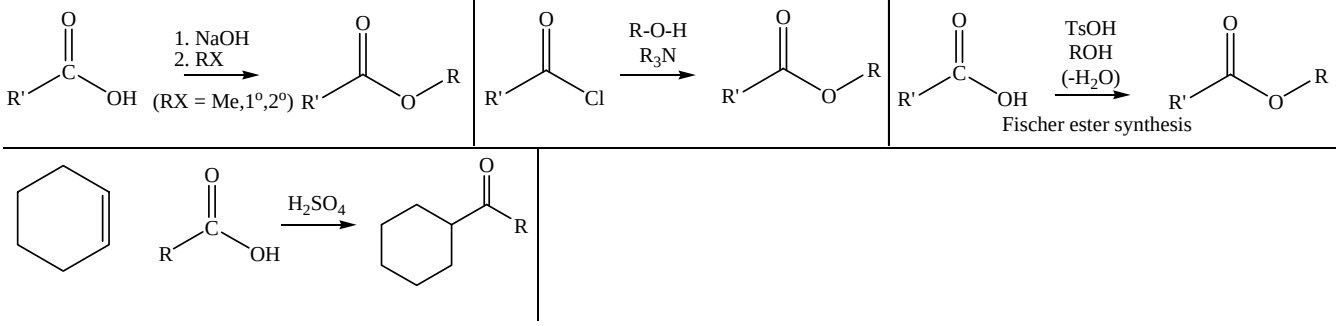


anhydride (RCO_2H)
ester (ROH)
1° amide (NH_3)
2° amide (RNH_2)
3° amide (R_2NH)
aldehyde (R_2AlH = DIBAH)
ketone (R_2Cu Li^+ = cuprate)

Esters



A few ways to make RCO_2R'

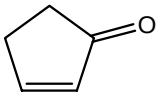


Products from reactions of carbon nucleophiles and carbon electrophiles used in our course:

Carbon and hydrogen nucleophiles

Carbon electrophiles	R: $^{\ominus}$ $Li^{\oplus}$ organolithium reagents	R: $^{\ominus}$ (MgBr)$^{\oplus}$ organolithium reagents	RCC$^{\ominus}$ $Na^{\oplus}$ acetylides	$Na^{\oplus}$ $^{\ominus}$:CN: cyanide	$R_2Cu^{\ominus}$ $Li^{\oplus}$ cuprates	$Li^{\oplus}$ $AlH_4^{\ominus}$ (LAH)	$Na^{\oplus}$ $BH_4^{\ominus}$	 diisobutylaluminium hydride (DIBAH)
methyl RX	NR	NR	alkynes	nitriles	2 RX coupling reaction	alkyls	alkyls	NR
primary RX	NR	NR	alkynes	nitriles	2 RX coupling reaction	alkyls	alkyls	NR
secondary RX	NR	NR	E2	nitriles	2 RX coupling reaction	alkyls	alkyls	NR
ethylene oxide	1° ROH	1° ROH	1° ROH alkynes	1° ROH nitriles	1° ROH	1° ROH	1° ROH	NR
propylene oxide	2° ROH	2° ROH	2° ROH alkynes	2° ROH nitriles	2° ROH	2° ROH	2° ROH	NR
isobutylene oxide	3° ROH	3° ROH	3° ROH alkynes	3° ROH nitriles	3° ROH	3° ROH	3° ROH	NR
methanal	1° ROH	1° ROH	1° ROH alkynes	cyanohydrin	NR	methanol	methanol	NR
simple aldehydes	2° ROH	2° ROH	2° ROH alkynes	cyanohydrin	NR	1° ROH	1° ROH	NR
simple ketones	3° ROH	3° ROH	3° ROH alkynes	cyanohydrin unless sterically hindered	NR	2° ROH	2° ROH	NR
simple esters	3° ROH (Nu: twice)	3° ROH (Nu: twice)	NR	NR	1° ROH (Nu: twice)	1° ROH	NR	aldehydes
simple carboxylic acids	ketones (B: once Nu: once)	acid/base no net rxn	acid/base no net rxn	NR	acid/base no net rxn	acid/base no net rxn	acid/base no net rxn	acid/base no net rxn
simple acid chlorides	3° ROH (Nu: twice)	3° ROH (Nu: twice)	NR	NR	ketones	1° ROH	1° ROH	NR
simple nitriles	ketones	ketones	NR	NR	NR	1° amines (also amines from amides)	NR	aldehydes (also aldehydes from 3° amides)
carbon dioxide	carboxylic acids	carboxylic acids	carboxylic acids	NR	NR	NR	NR	NR
α,β-unsaturated ketones	3° ROH	3° ROH	NR	NR	conjugate addition	alcohols	alcohols	NR

WK = normal workup to neutralize the reaction conditions. For the basic reactions (like above) above this would require mild acid neutralization (H_3O^+).
NR = no reaction or no productive result or not emphasized

	$R'^{\ominus}\ Li^{\oplus}$	$R'^{\ominus}\ (MgHBrH)^{\oplus}$	$R'_2Cu^{\ominus}\ Li^{\oplus}$	$RCC^{\ominus}\ Na^{\oplus}$	$NC^{\ominus}\ Na^{\oplus}$	$Li^{\oplus}\ AlH_4^{\ominus}$	$Na^{\oplus}\ BH_4^{\ominus}$
1^o RCH_2Br primary RX	NA	NA	**alkyl coupling**	alkyne	nitriles	1^o RCH_2-H	1^o RCH_2-H
2^o R_2CHBr secondary RX	NA	NA	**alkyl coupling**	E2	nitriles	2^o R_2CH-H	2^o R_2CH-H
 epoxides	ROH (+2C+OH)	ROH (+2C+OH)	ROH (+2C+OH)	ROH (+2C+OH)	ROH (+2C+OH)	ROH	ROH
$H_2C{=}O$ methanal	1^o ROH	1^o ROH	NA	1^o ROH	1^o ROH	methanol	methanol
$RHC{=}O$ aldehydes	2^o ROH	2^o ROH	NA	2^o ROH	2^o ROH	1^o ROH	1^o ROH
$R_2C{=}O$ ketones	3^o ROH	3^o ROH	NA	3^o ROH	3^o ROH	2^o ROH	2^o ROH
$O{=}C{=}O$ carbon dioxide	carboxylic acids	carboxylic acids	NA	NA	NA	NA	NA
RCO_2R' esters	3^o ROH (twice)	3^o ROH (twice)	NA	NA	NA	1^o ROH	**NA**
RCO_2H carboxylic acids	ketones acid/base x 1 nucleophile x 1	NA	NA	acid/base	acid/base	1^o ROH	**NA**
$R{-}C{\equiv}N$ nitrils	ketones	ketones	NA	NA	NA	1^o RNH_2	**NA**
$RCONR_2$ 3^o amides	ketones	ketones	NA	NA	NA	1^o,2^o,3^o RNH_2	**NA**
RCOCl acid chlorides	3^o ROH	3^o ROH	ketones	NA	NA	1^o ROH	**NA**
 α,β-unsaturated carbonyls	1,2-addition	1,2-addition	**conjugate addition (1,4-addition)**	1,2-addition	**conjugate addition (1,4-addition)**	1,2-addition	**NA**

WK = workup reaction with electrophilic/acidic H_3O^+

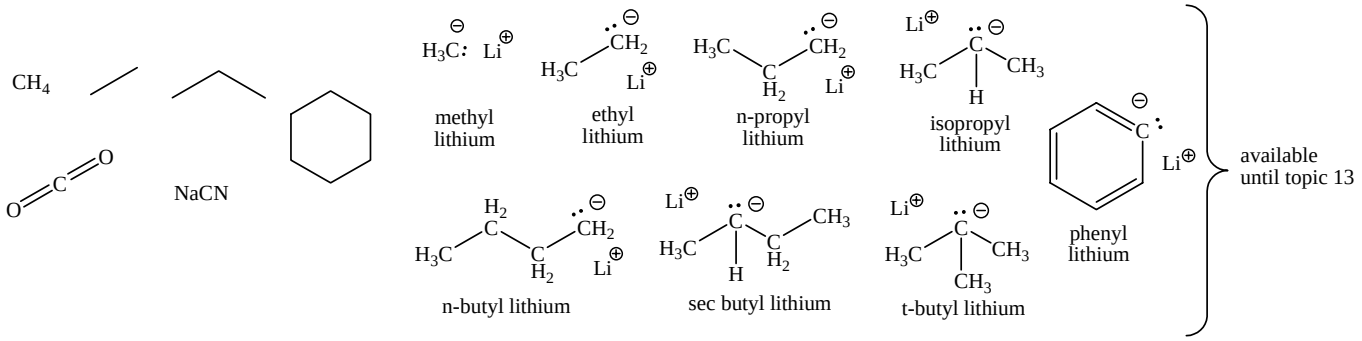
NA = not applicable to our course (no reaction, not productive or not emphasized)

Use clues in the target molecule to determine what the last step could have been. Once you work back one step, use clues in that molecule to determine how you could work back one additional step. Repeat this process until you get to the necessary starting conditions

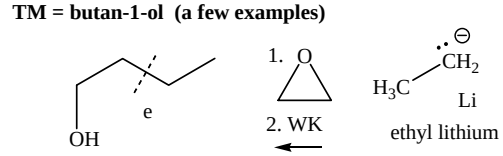
Some points to remember:

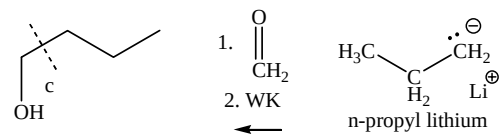
1. OH can be oxidized to aldehydes (from 1° ROH) or carboxylic acids (from 1°ROH, which can be made into esters or acid chlorides and more), or ketones (from 2° ROH).
2. OH can be made into a leaving group (Cl, Br, I, OTs), which can be made into amines, esters, nitriles, ethers, alkynes, thiols, thioethers, replaced with "H/D" and much more.
3. OH can be eliminated in H_2SO_4/Δ, but rearrangements could be a problem. Br can be eliminated with potassium t-butoxide, but regioselectivity can be a problem (requires anti C_β-H/C_α-X conformation).

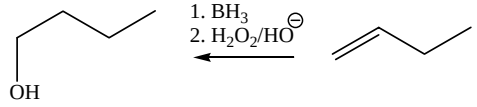
Starting Structures:

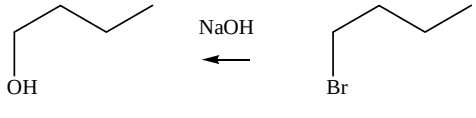


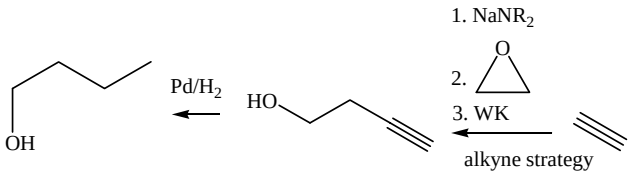
TM = butan-1-ol (a few examples)

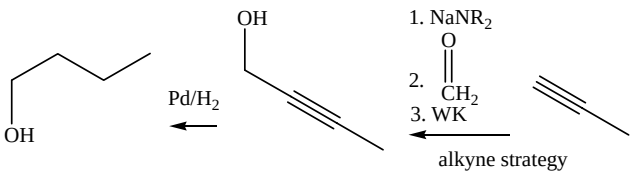




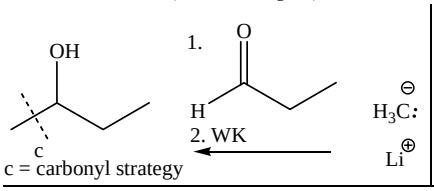


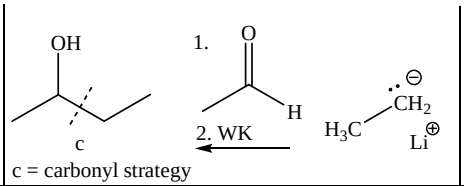


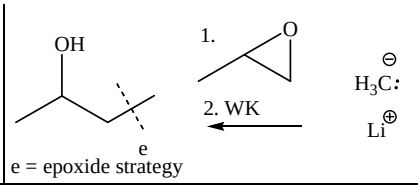


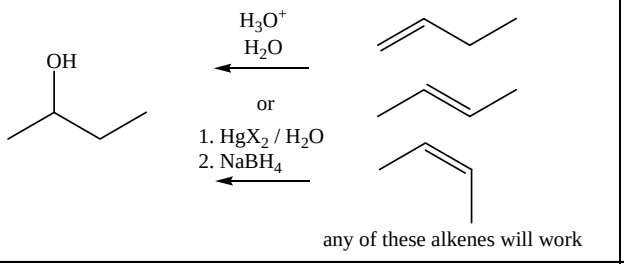


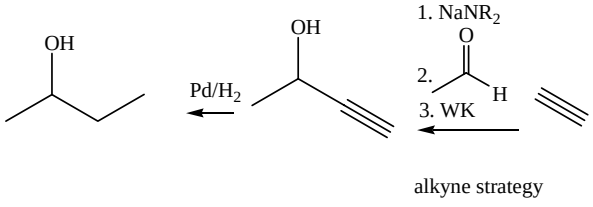
TM = butan-2-ol (a few examples)











Alkene reactions

1 unsubstituted alkene

2 monosubstituted alkene

3 monosubstituted alkene

4 trans disubstituted alkene

5 cis disubstituted alkene

6 cis disubstituted alkene

7 gem disubstituted alkene

8 gem disubstituted alkene

9 trisubstituted alkene

10 tetrasubstituted alkene

11 12 alkyne patterns

---

reaction conditions H_2SO_4 / H_2O

1 2 3 4 R & S 5 6 R & S

7 8 9 R & S 10 RS, SR, RR, SS 11 12

---

reaction conditions TsOH / ROH

1 2 3 4 R & S 5 6 R & S

7 8 9 R & S 10 RS, SR, RR, SS 11 NA 12 NA

---

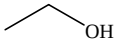
reaction conditions HBr (HCl, HI are similar)

1 2 3 rearrangement 4 R & S 5 6 R & S

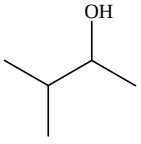
7 8 9 R & S 10 RS, SR, RR, SS 11 12 E & Z

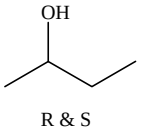
---

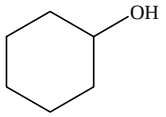
reaction conditions: 1. $Hg(OAc)_2/H_2O$ 2. $NaBH_4$ (avoids rearrangements)

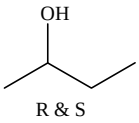
1 

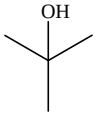
2 

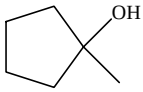
3 
NO rearrangement

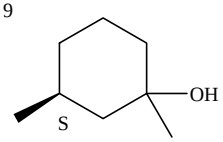
4 
R & S

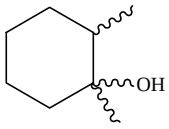
5 

6 
R & S

7 

8 

9 
R & S

10 
RS, SR, RR, SS

11 NA

12 NA

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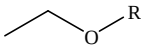
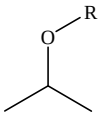
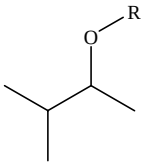
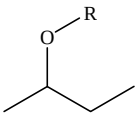
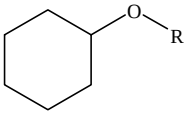
reaction conditions: 1. $Hg(OAc)_2/ROH$ 2. $NaBH_4$ (avoids rearrangements)

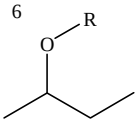
1 

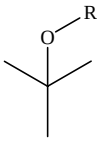
2 

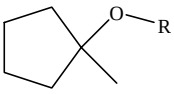
3 
NO rearrangement

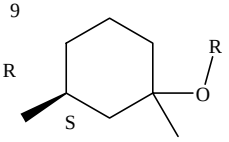
4 
R & S

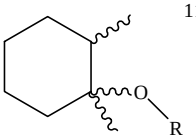
5 

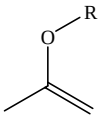
6 
R & S

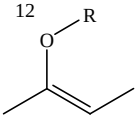
7 

8 

9 
R & S

10 
RS, SR, RR, SS

11 
vniyl ether

12 
E & Z
vniyl ether

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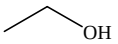
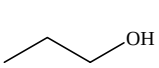
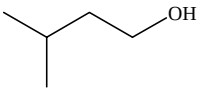
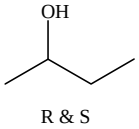
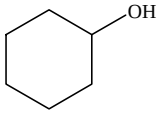
reaction conditions: 1. $(BH_3)_2$ 2. $H_2O_2 / HO^{\ominus}$ diborane for alkenes; 1. R_2BH 2. $H_2O_2 / HO^{\ominus}$ dialkylborane for alkynes; anti-Markovnikov addition

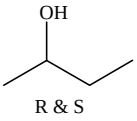
1 

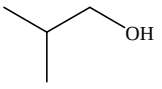
2 

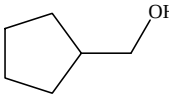
3 
NO rearrangement

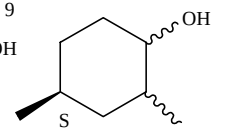
4 
R & S

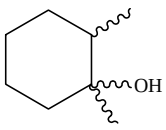
5 

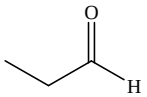
6 
R & S

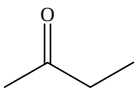
7 

8 

9 
RS, SR, RR, SS

10 
RS, SR, RR, SS

11 

12 

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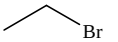
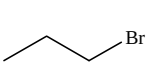
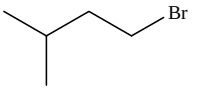
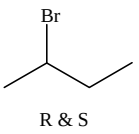
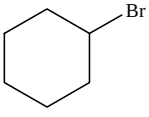
reaction conditions: 1. $(BH_3)_2$ 2. $Br_2 / CH_3O^{\ominus}$ diborane for alkenes; 1. R_2BH 2. $Br_2 / CH_3O^{\ominus}$ dialkylborane for alkynes; anti-Markovnikov addition

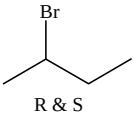
1 

2 

3 
NO rearrangement

4 
R & S

5 

6 
R & S

7

8

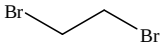
9
RS, SR, RR, SS

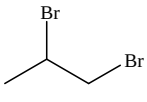
10
RS, SR, RR, SS

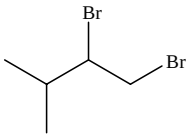
11
vniyl bromide

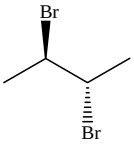
12
vniyl bromide

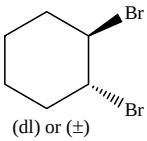
reaction conditions Br_2 (Cl_2 is similar) anti-addition

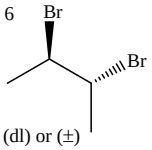
1 

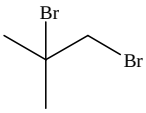
2 

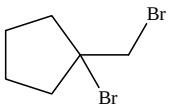
3 
NO rearrangement

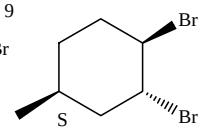
4 
meso (achiral)

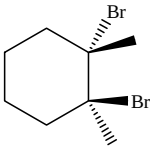
5 
(dl) or (±)

6 
(dl) or (±)

7 

8 

9 
RR & SS

10 
RR & SS

11 NA

12 NA

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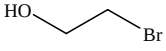
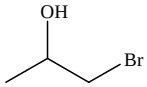
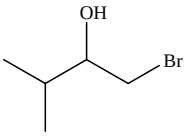
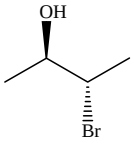
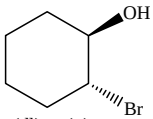
reaction conditions Br_2 / H_2O (Cl_2 / H_2O is similar) anti-addition / Markovnikov addition Can form epoxides with NaOH.

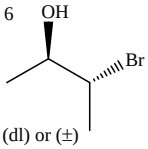
1 

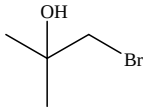
2 

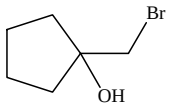
3 
NO rearrangement

4 
meso (achiral)

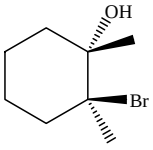
5 
(dl) or (±)

6 
(dl) or (±)

7 

8 

9 NA

10 
RR & SS

11 NA

12 NA

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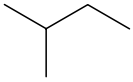
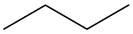
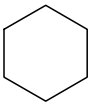
reaction conditions Pd / H_2 palladium & hydrogen syn-addition

1 

2 

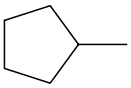
3 

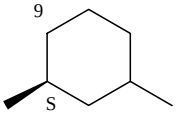
4 

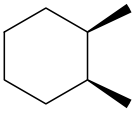
5 

6 

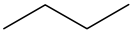
7 

8 

9 
R & S

10 
meso

11 

12 

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reaction conditions Pd / H_2 palladium & hydrogen syn-addition

1 no reaction

2 no reaction

3 no reaction

4 no reaction

5 no reaction

6 no reaction

7 no reaction

8 no reaction

9 no reaction

10 no reaction

11 

12 

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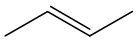
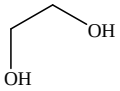
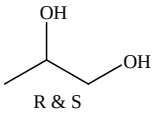
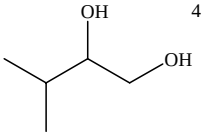
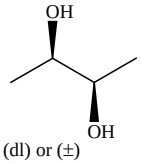
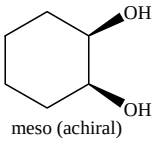
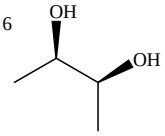
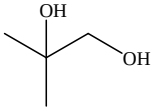
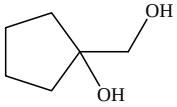
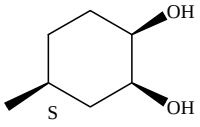
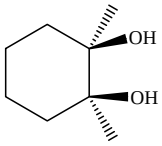
reaction conditions: Na / NH_3 in ammonia — anti-addition

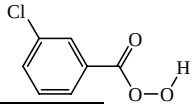
1	2	3	4	5	6
no reaction	no reaction	no reaction	no reaction	no reaction	no reaction

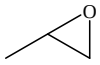
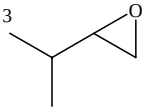
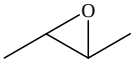
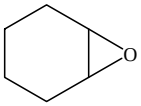
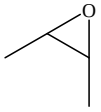
7	8	9	10	11	12
no reaction	no reaction	no reaction	no reaction	no reaction	

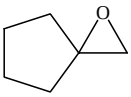
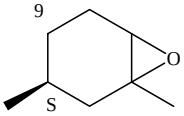
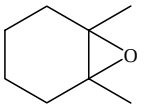
reaction conditions: $KMnO_4$ or OsO_4 — potassium permanganate osmium tetroxide — syn-addition

1	2	3	4	5	6
	 R & S	 NO rearrangement	 (dl) or (±)	 meso (achiral)	 meso (achiral)

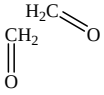
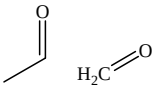
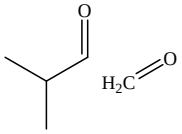
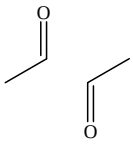
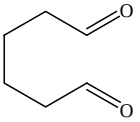
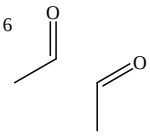
7	8	9	10	11	12
		 cis and trans to methyl	 meso (achiral)	NA	NA

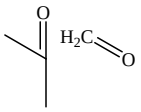
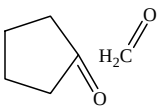
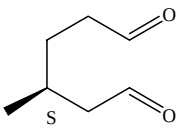
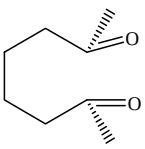
reaction conditions:  — meta chloroperbenzoic acid (mCPBA) — syn-addition

1	2	3	4	5	6
	 R & S	 R & S	 RR & SS	 RS & SR	 RS & SR

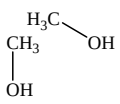
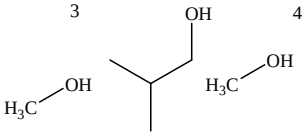
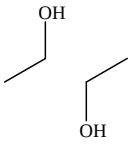
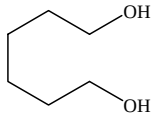
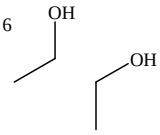
7	8	9	10	11	12
		 cis and trans to methyl	 RS & SR		

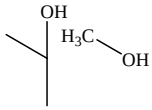
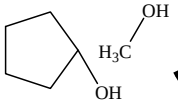
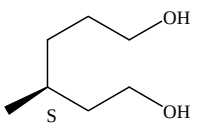
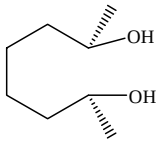
reaction conditions: 1. O_3, -78°C; 2. CH_3SCH_3 — cleaves double bone into two C=O groups (aldehydes or ketones)

1	2	3	4	5	6
					

7	8	9	10	11	12
				NA	NA

reaction conditions: 1. O_3, -78°C; 2. $NaBH_4$ — cleaves double bone into two alcohol groups

1 
2 
3 
4 
5 
6 

7 
8 
9 
10 
11 NA
12 NA

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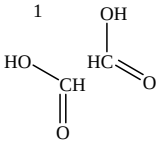
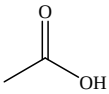
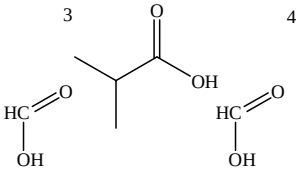
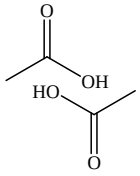
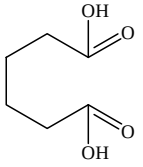
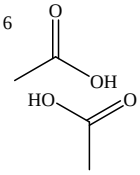
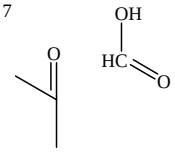
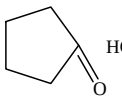
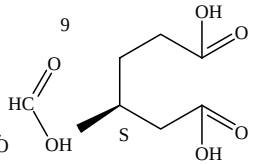
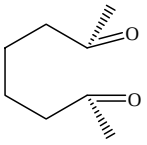
reaction conditions: 1. O_3, -78°C; 2. H_2O_2, $HO^{\ominus}$ — cleaves double bone into two C=O groups (acids or ketones)

1 
2 
3 
4 
5 
6 

7 
8 
9 
10 
11 NA
12 NA

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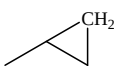
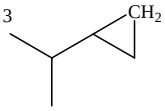
reaction conditions: CH_2I_2, Zn / Cu; Simmons Smith reagent — syn-addition

1 
2 
R & S
3 
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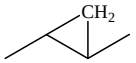
4 
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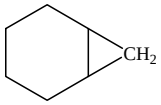
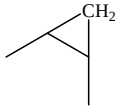
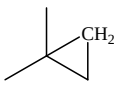
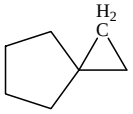
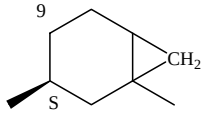
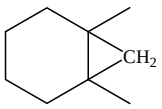
5 
RS & SR
6 
RS & SR

7 
8 
9 
cis and trans to methyl
10 
RS & SR
11 NA
12 NA

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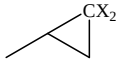
reaction conditions: CH_2I_2, Zn / Cu; Simmons Smith reagent — syn-addition — X = Br or Cl

1 
2 
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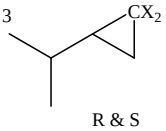
3 
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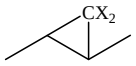
4 
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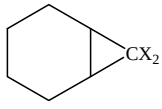
5 
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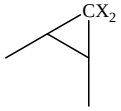
6 
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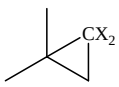
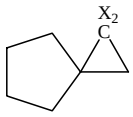
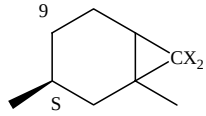
7 
8 
9 
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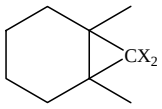
10 
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