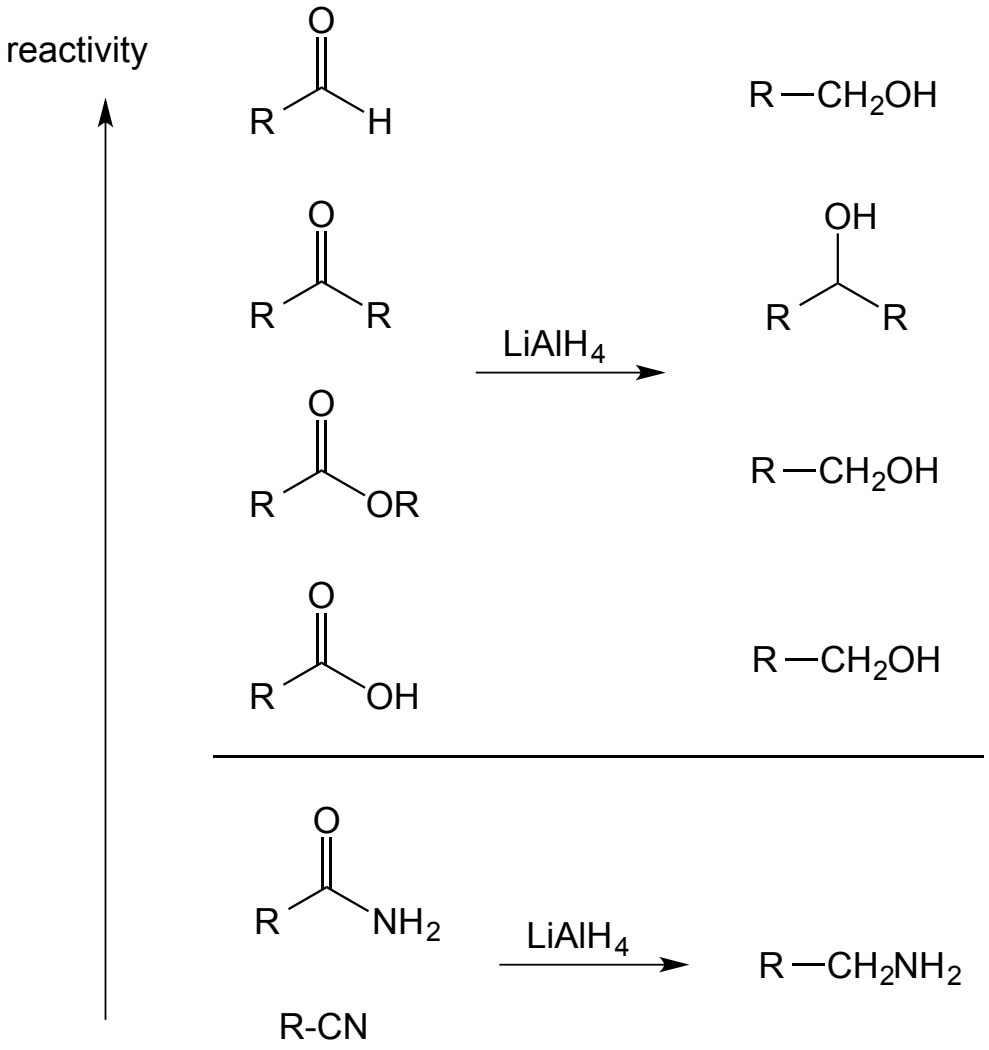
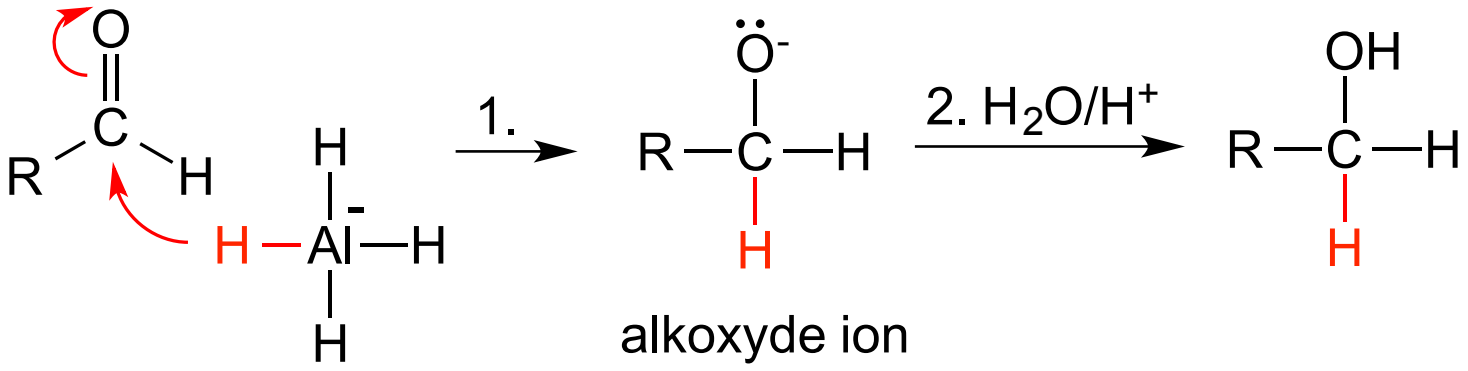
FUNCTIONAL GROUP TRANSFORMATIONS

Selective reductions of oxo compounds and carboxylic acid derivatives

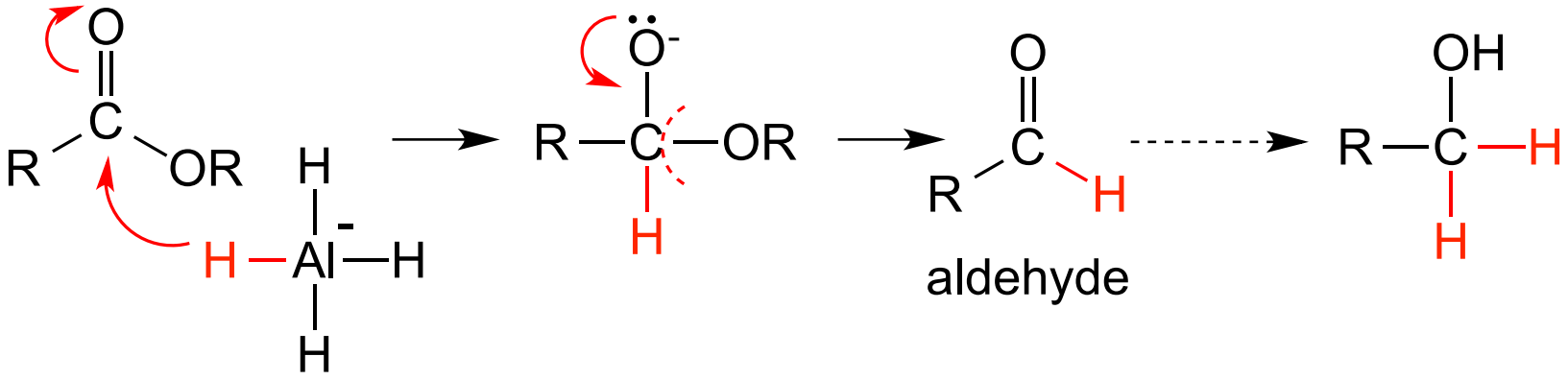


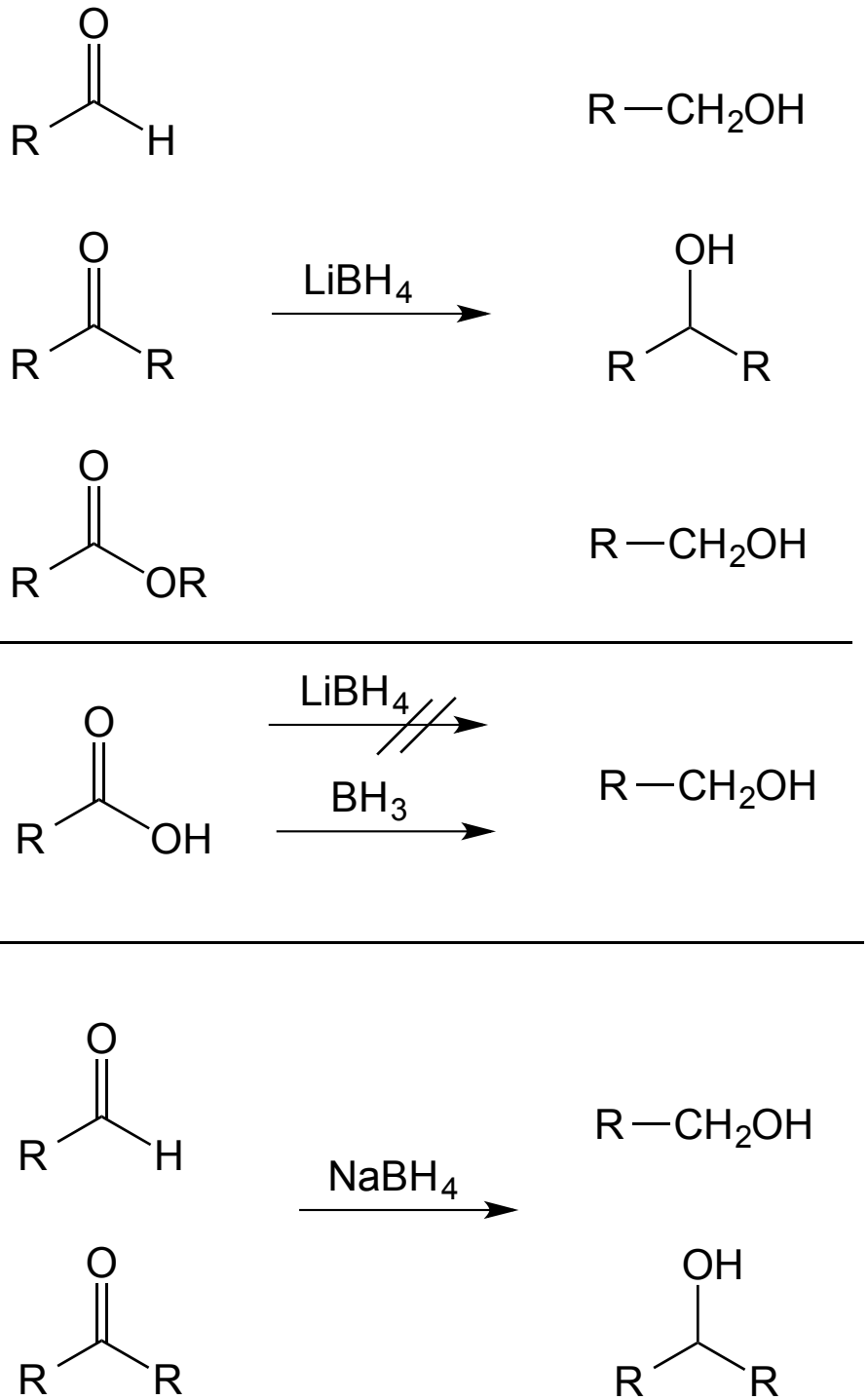
Mechanism

Reduction of oxo compounds

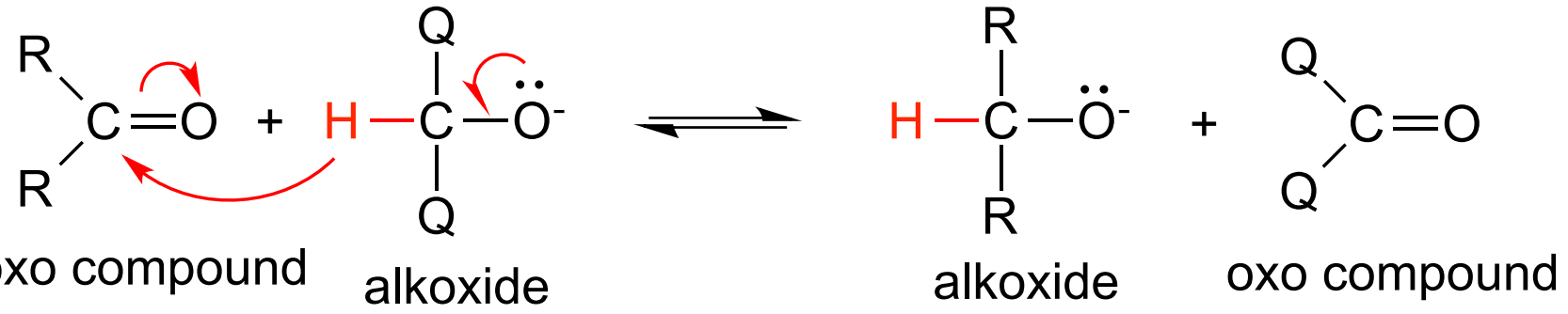


Reduction of esters

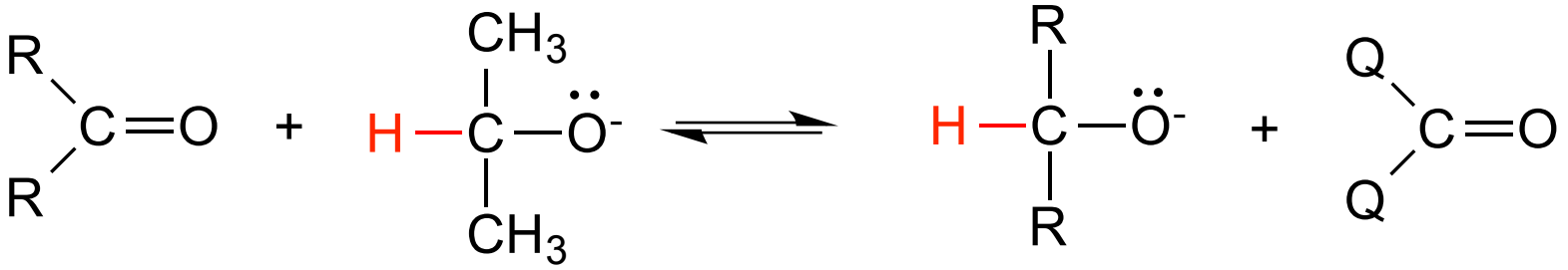



O
R
H
R—CH2OH
O
R
R
LiBH4
OH
R
R
O
R
OR
R—CH2OH
LiBH4
O
R
OH
BH3
R—CH2OH
O
R
H
NaBH4
R—CH2OH
O
R
R
OH
R
R

Reduction with aluminium isopropylate
(Meerwein-Ponndorf-Verley reduction)

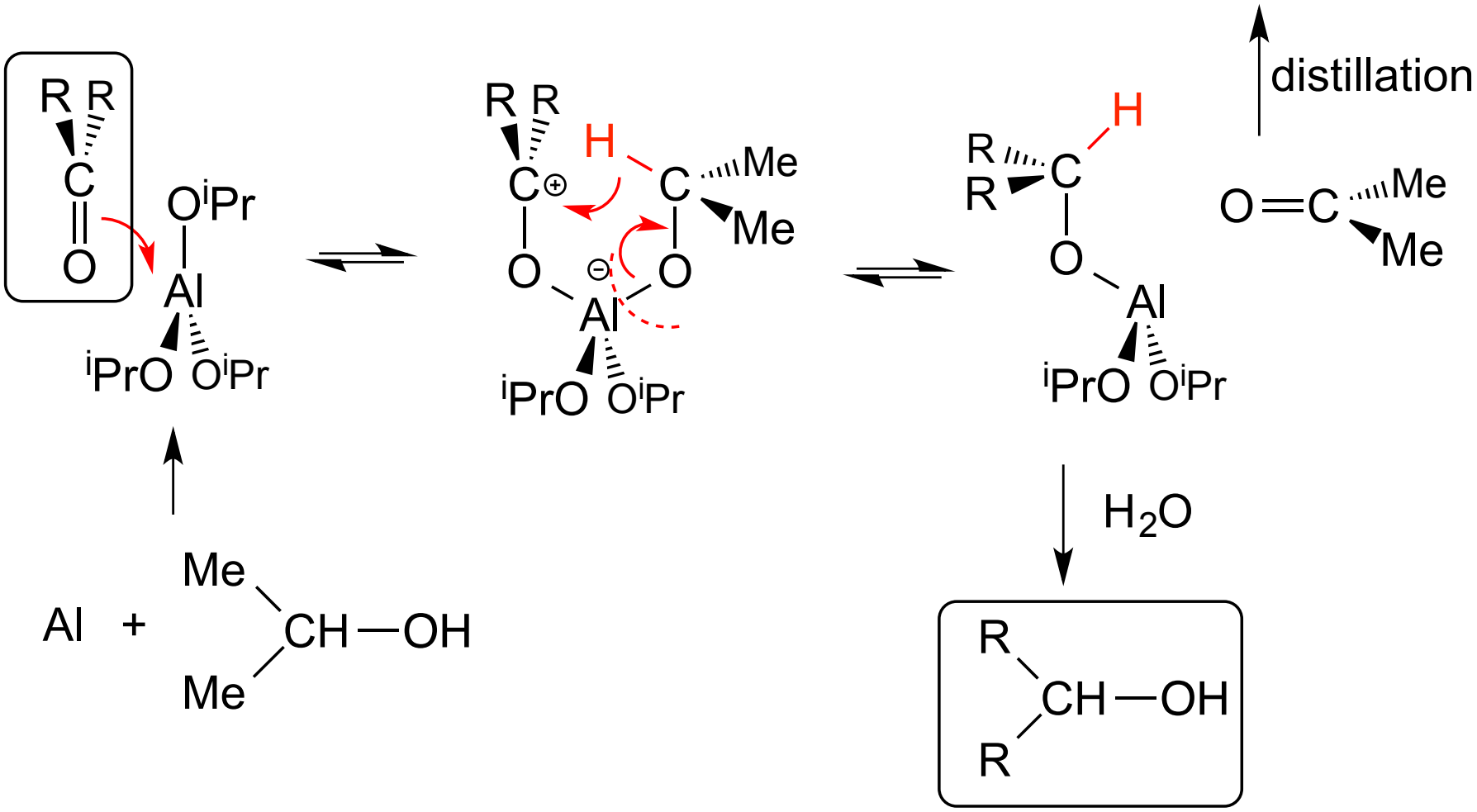


oxo compound alkoxide alkoxide oxo compound

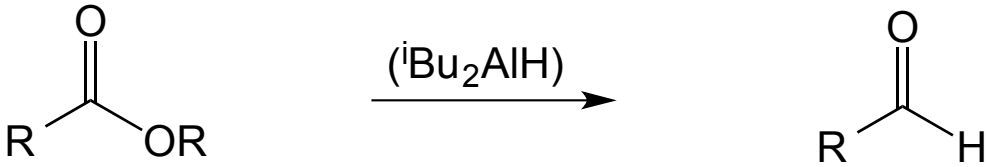


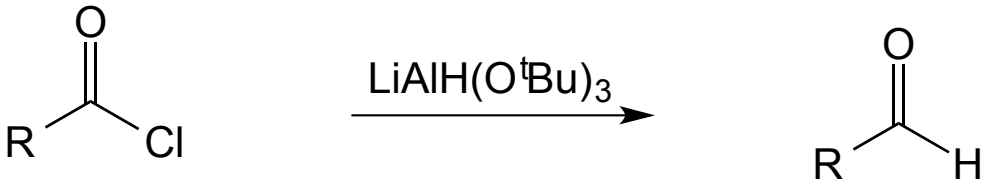
oxo compound isopropylate anion alkoxide acetone

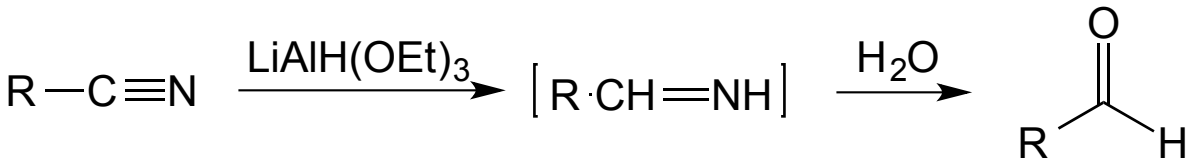
Mechanism


R R
C
O
O^{i}Pr
Al
^{i}PrO O^{i}Pr
H
C
Me
Me
O
Al
^{i}PrO O^{i}Pr
R
R
C
H
O
Al
^{i}PrO O^{i}Pr
distillation
O=C
Me
Me
H_2O
Al +
Me
CH—OH
Me
R
CH—OH
R

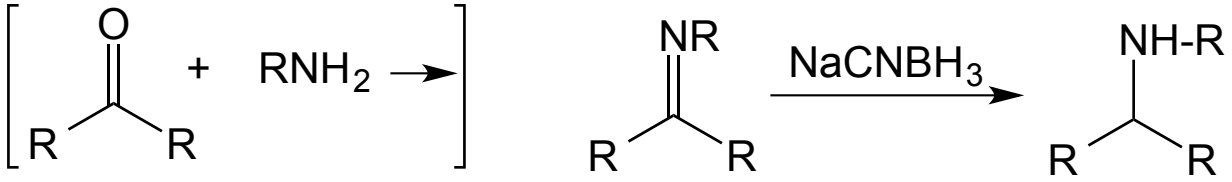
Reduction of carboxylic acid derivatives to aldehydes





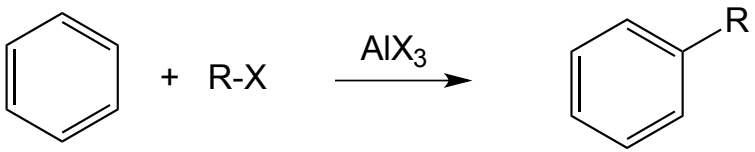


Reduction of Schiff bases (synthesis of secondary amines)

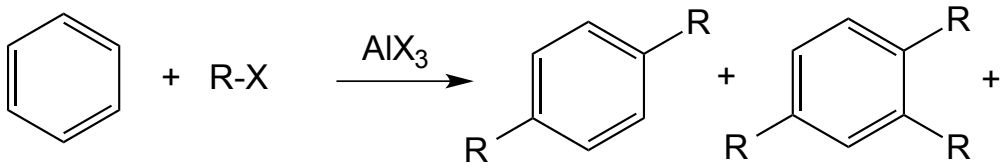


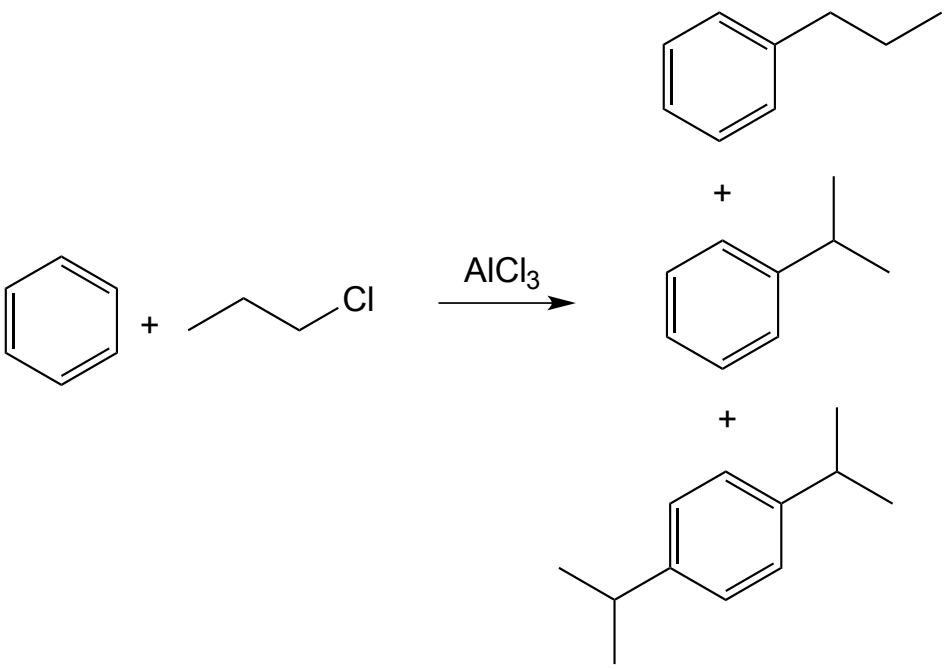
Functionalization of aromatic compounds

Friedel-Crafts alkylation

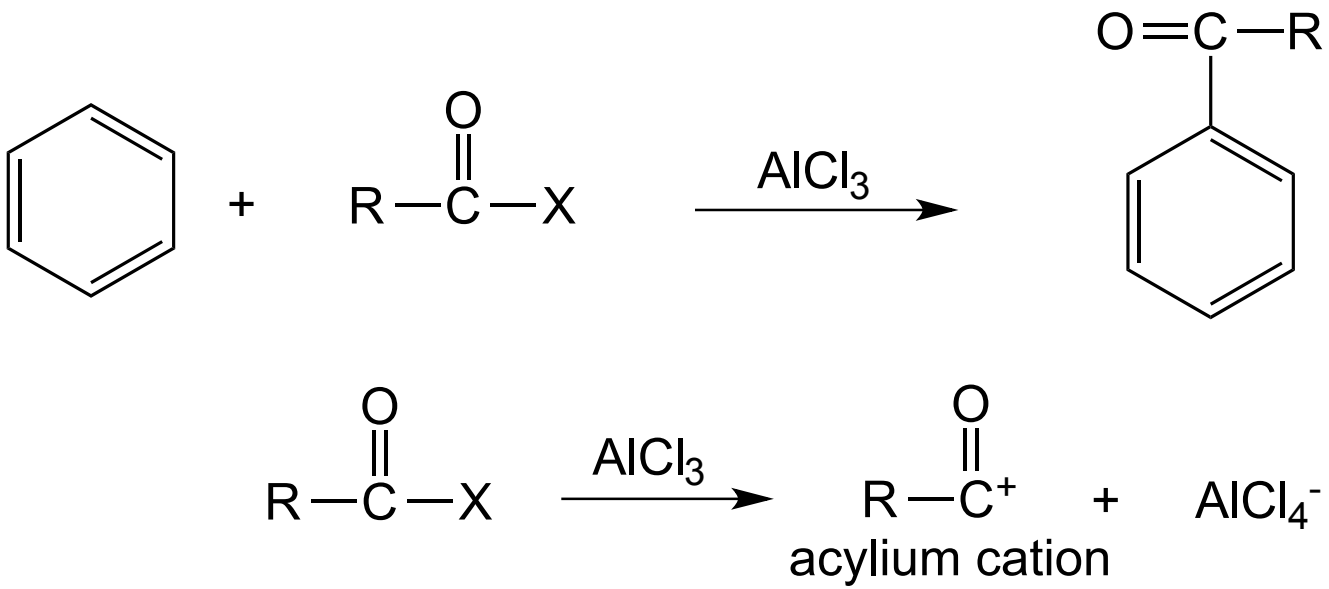


Difficulties

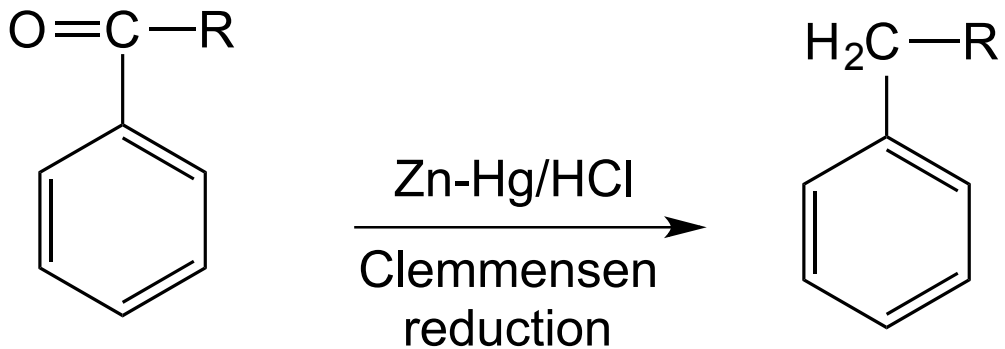




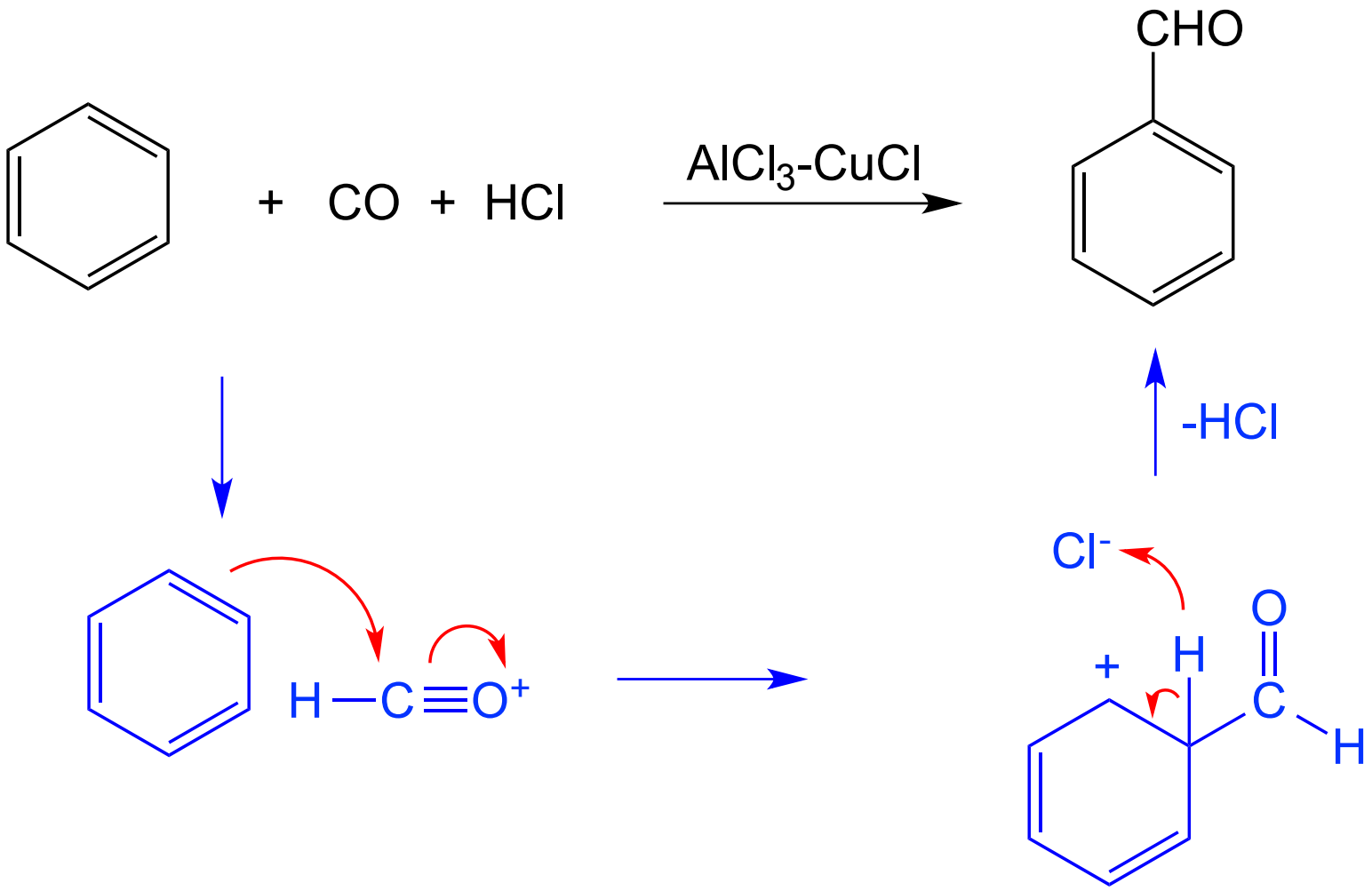
Friedel-Crafts acylation



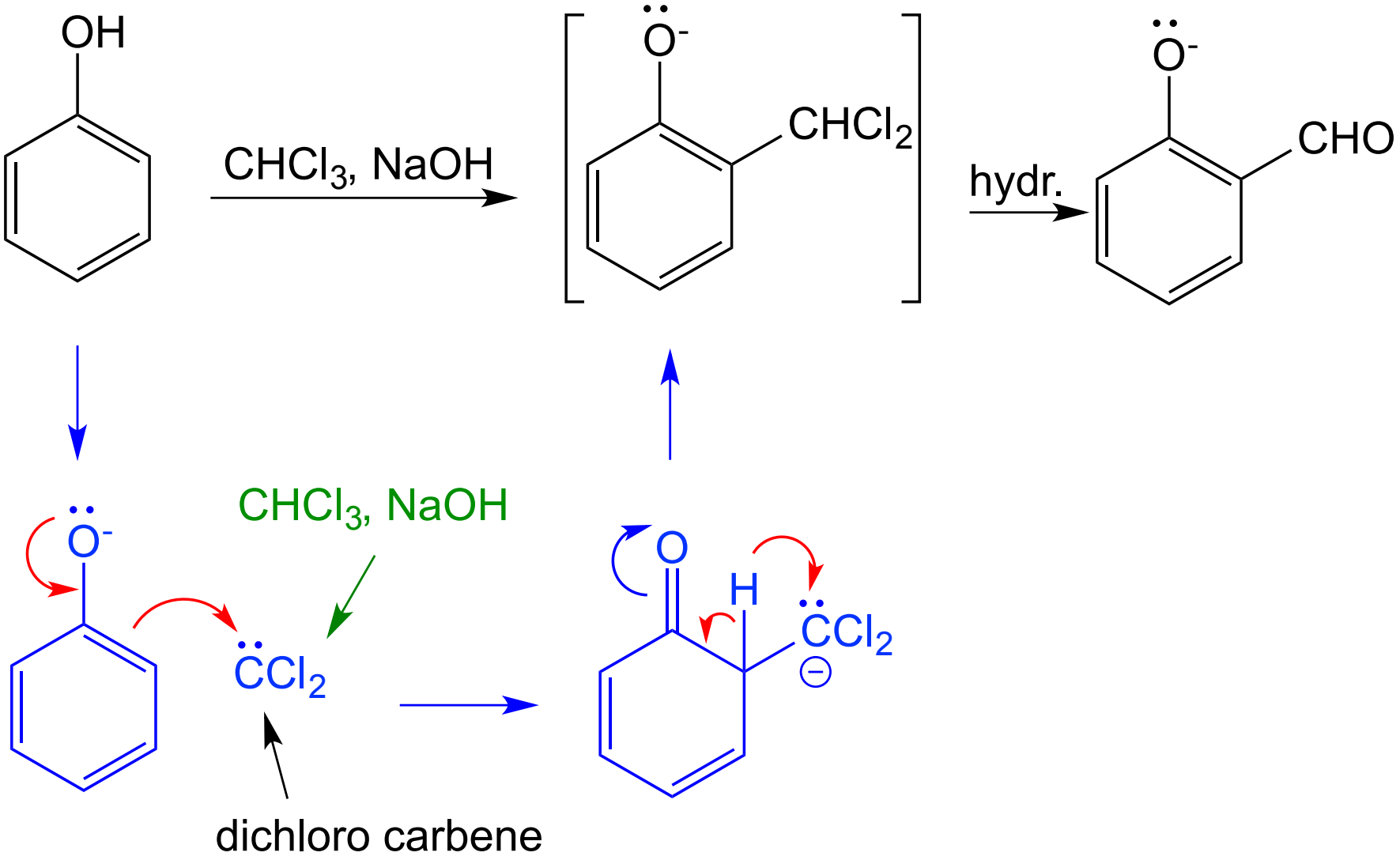
reduction of ketone



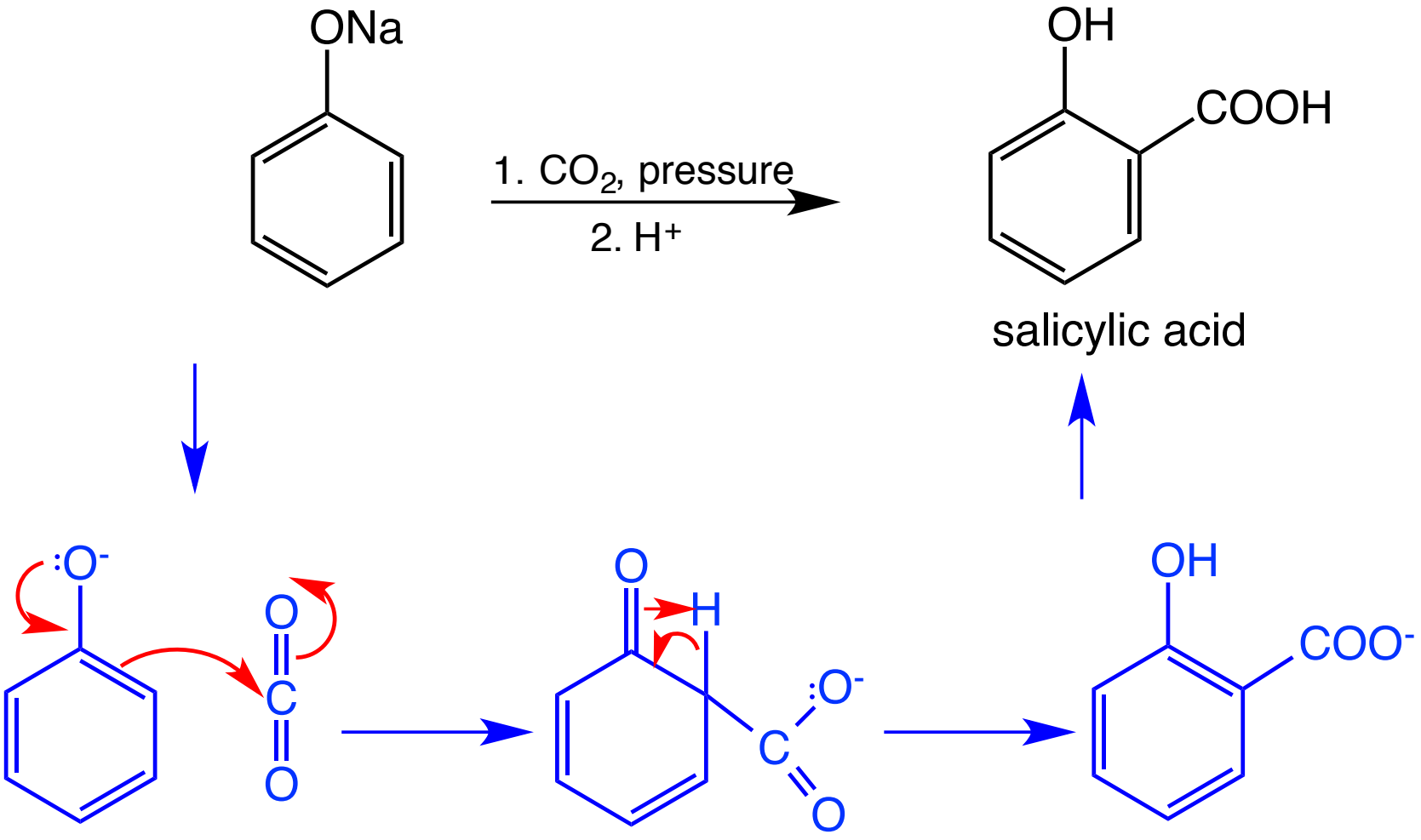
Gatterman-Koch synthesis (formylation of aromatic compounds)



Reimer-Tiemann reaction (formylation of phenols)

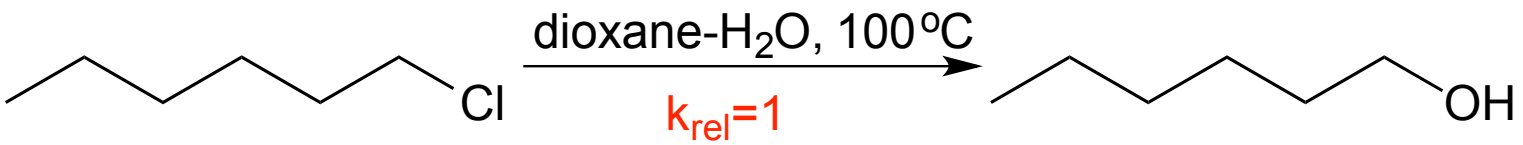


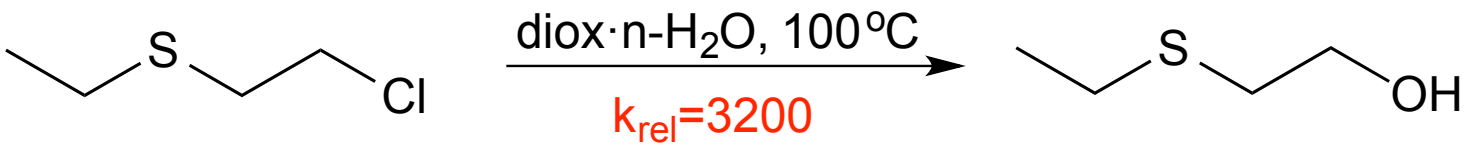
Kolbe-Schmidt reaction (carboxylation of phenols)



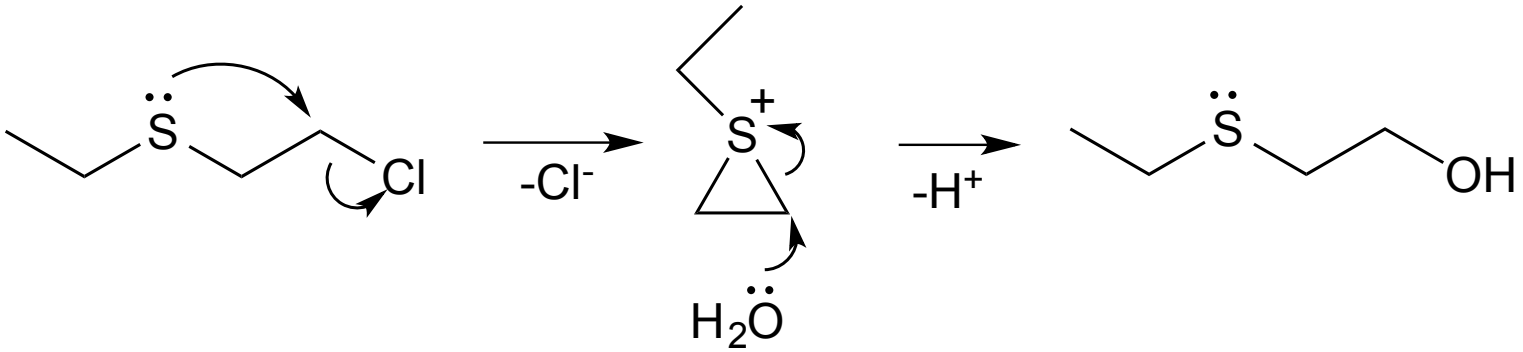
Reactions involving more than one functional groups

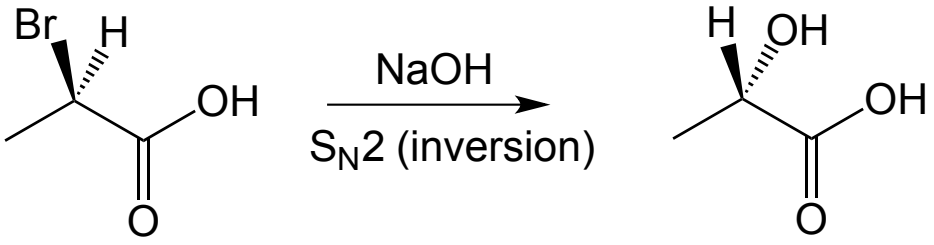
Neighboring group participation



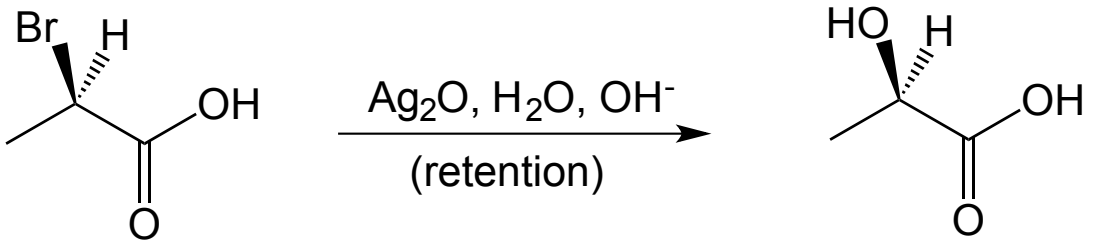


Mechanism

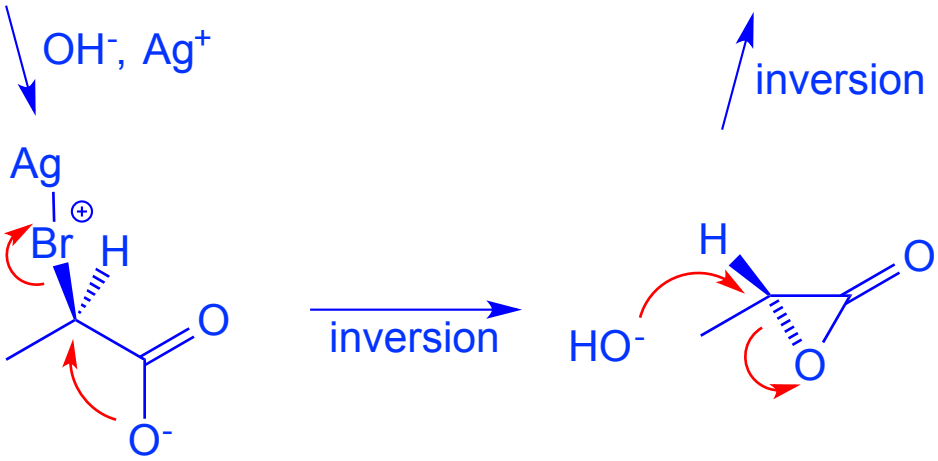




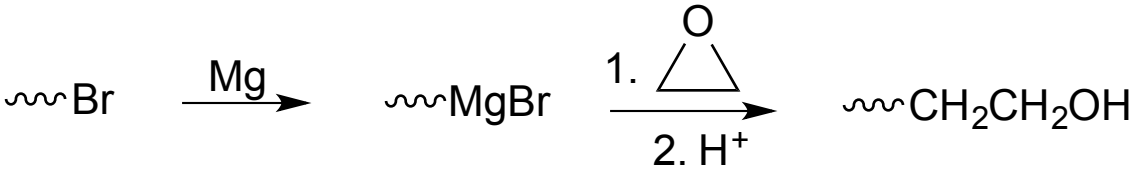
(*R*)-2-bromopropionic acid (*S*)-lactic acid

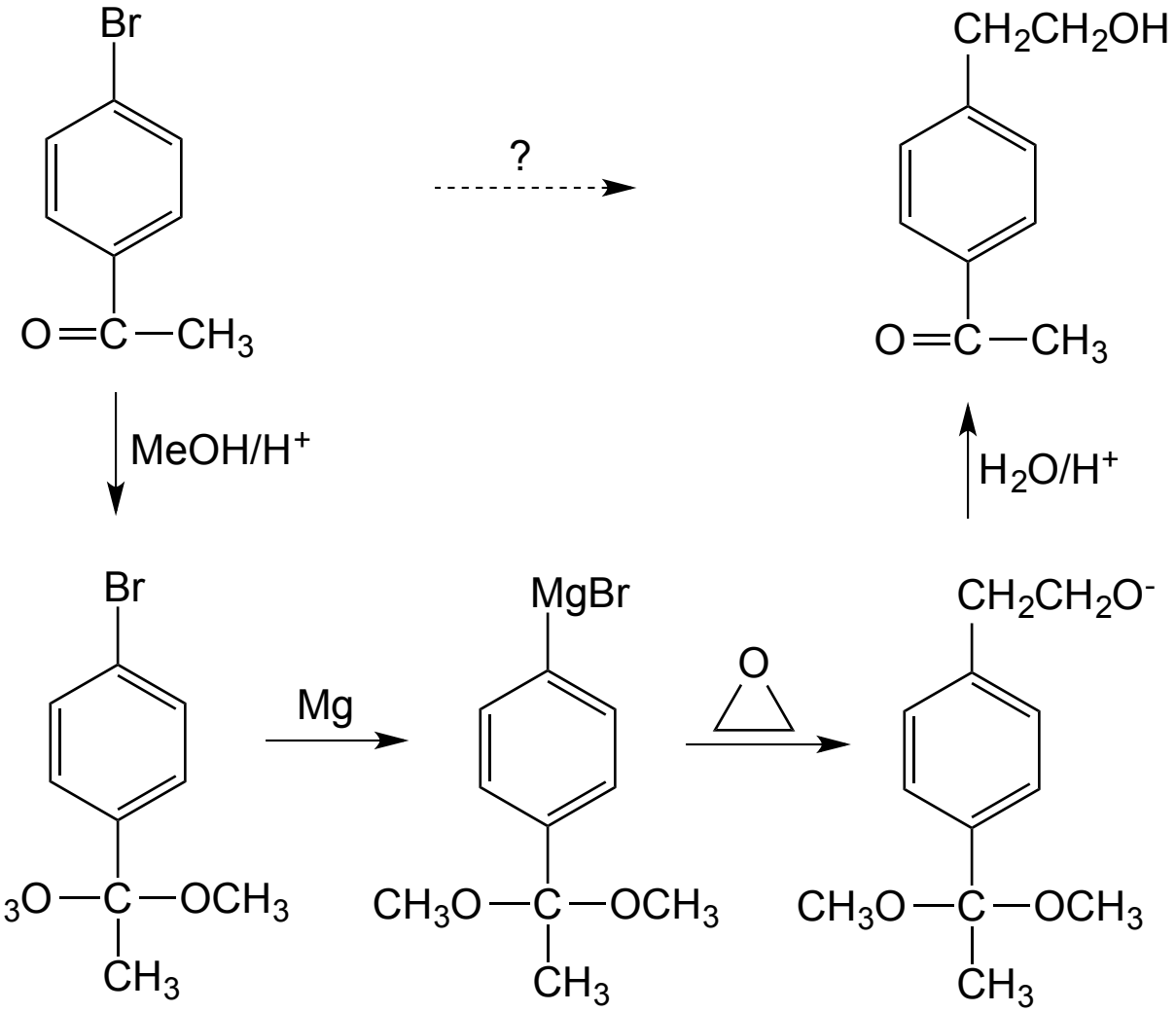


(*R*)-2-bromopropionic acid (*R*)-lactic acid

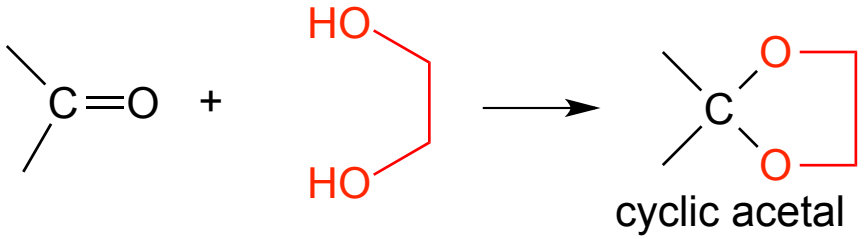


Selective protection of functional groups





Protection of carbonyl groups



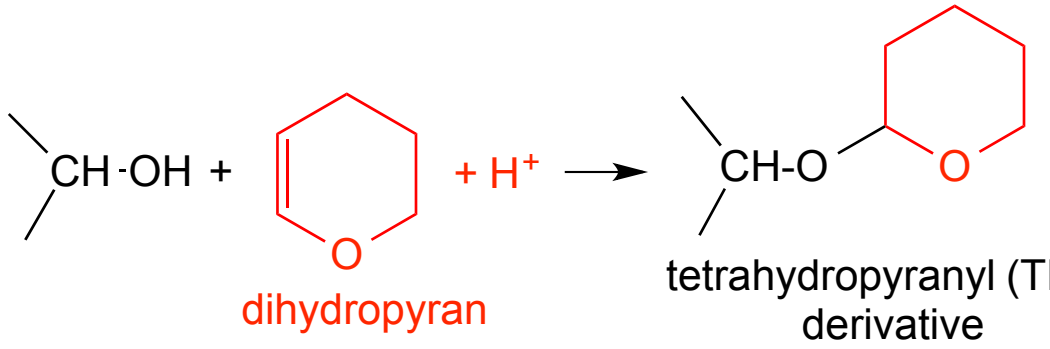
removal

H_2O/H^+

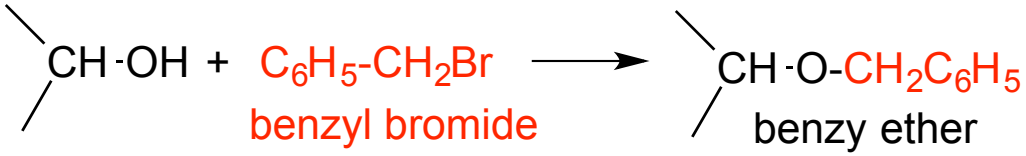
Protection of hydroxyl group

removal

H_2O/H^+

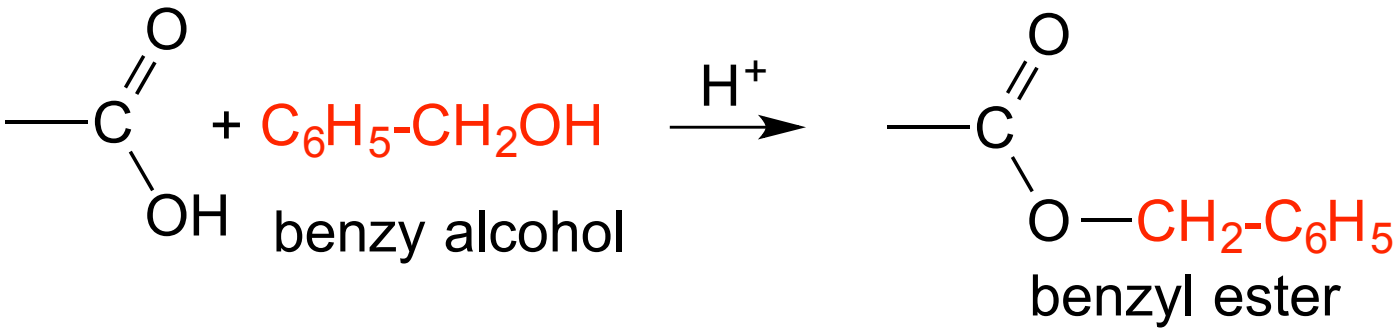


H_2O/H^+



H_2/Pd

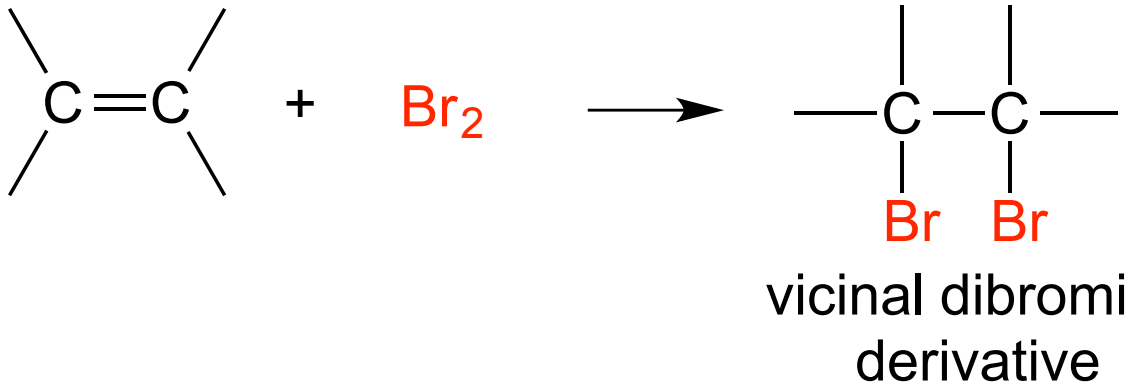
Protection of carboxyl group



removal

H_2/Pd

Protection of C=C double bond



NaI or Zn

Protection of amino group

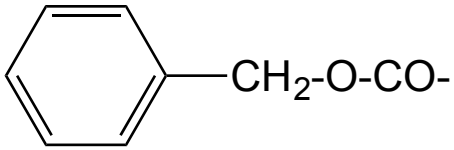
removal

$-NH_2$ + Z-Cl ⟶ -NH-Z — H_2/Pd

$-NH_2$ + Boc_2O ⟶ -NH-Boc — HCl-MeOH or CF_3COOH

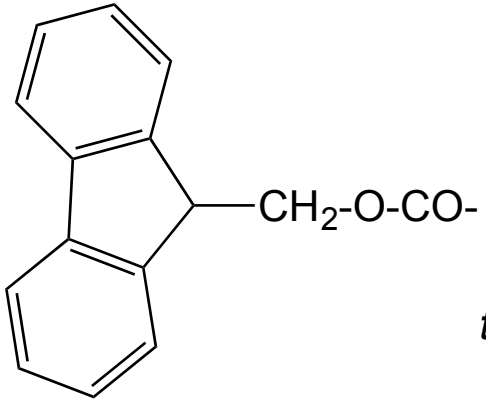
$-NH_2$ + Fmoc-Cl ⟶ -NH-Fmoc — nucleophile e.g. piperidine

$-NH_2$ ⟶ -NH-CO-O- carbamate or uretane



Z

benzyloxycarbonyl



Fmoc

fluorenylmethyleneoxycarbonyl

$(CH_3)_3C$-O-CO-

Boc

tert-butyloxycarbonyl