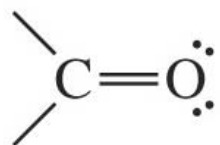


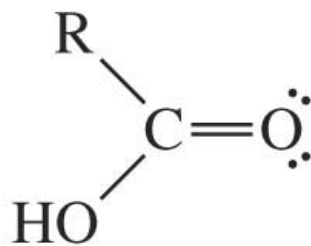
第12章醇及carbonyl (C=O) 化合物間的轉化：氧化, 還原, 及金屬有機(organometallic)試劑介紹

1) carbonyl (C=O) 化合物的還原反應

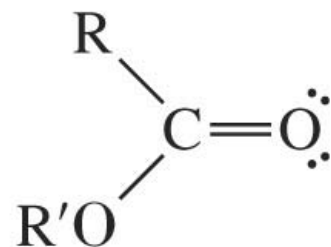
a)



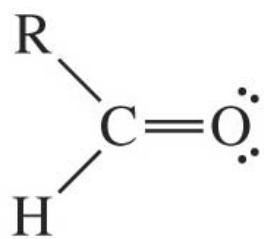
The carbonyl group



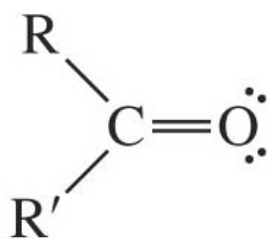
A carboxylic acid



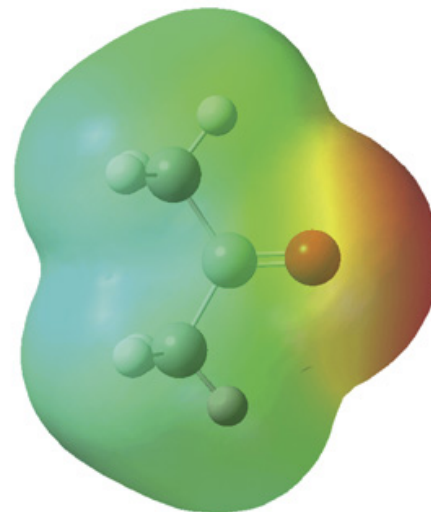
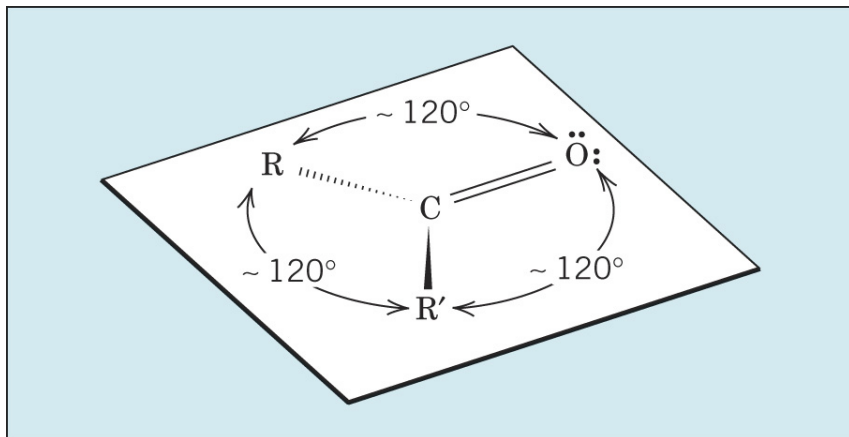
A carboxylate ester



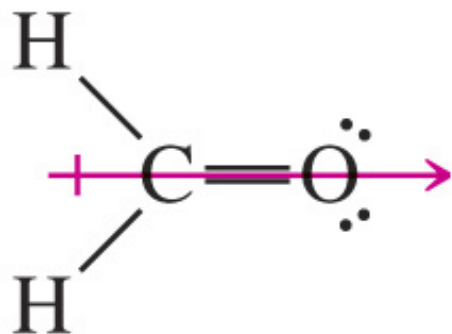
An aldehyde



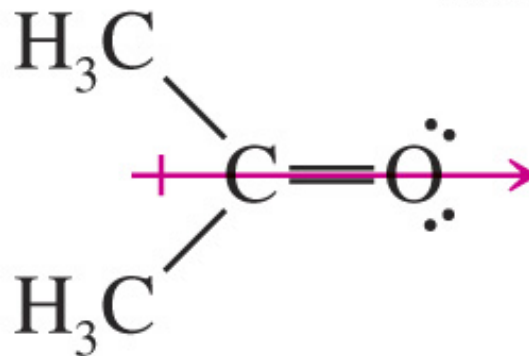
A ketone



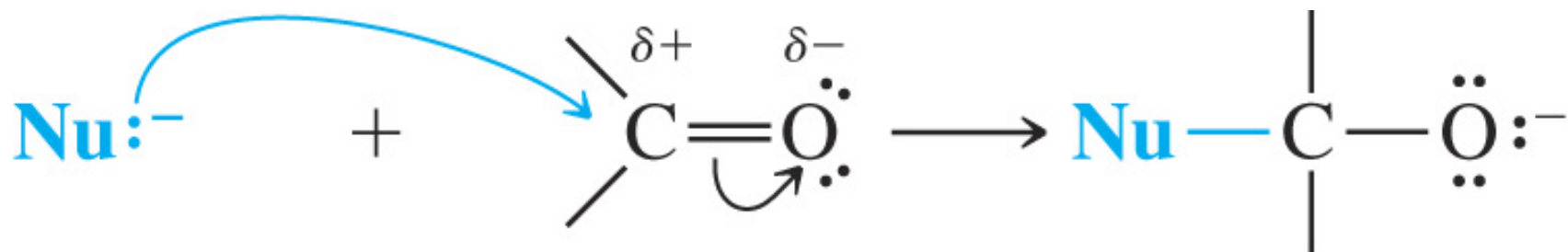
An electrostatic potential map for acetone



Formaldehyde
 $\mu = 2.27 \text{ D}$



Acetone
 $\mu = 2.88 \text{ D}$

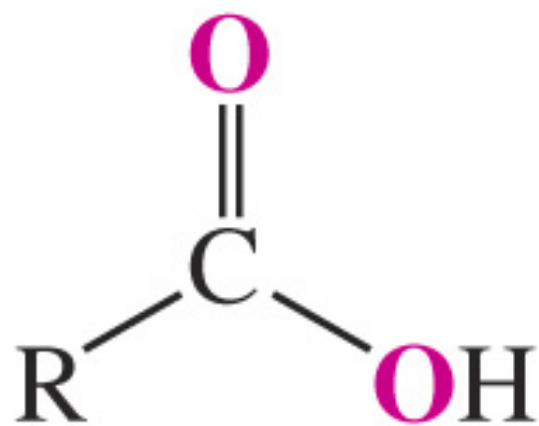


本章要介紹的親核試劑共有四種，即NaBH₄, LiAlH₄, RLi, RMgX；前兩種使得carbonyl化合物被還原，（be reduced）；而後兩種則與Carbonyl發生親核加成反應。所有這些反應都產生alcohols.

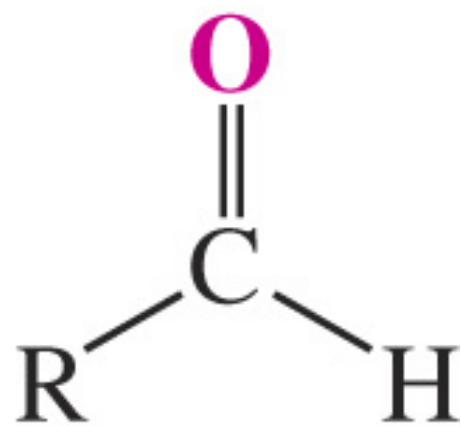
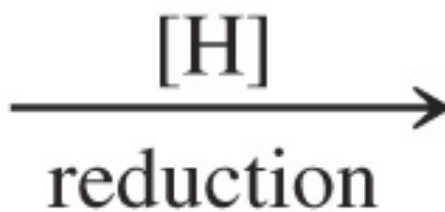
b) 還原反應：還原反應(reduction)的定義是有機分子在還原劑(reducing reagent)的作用下，發生氫原子數增加或氧原子數減少的反應。(Reduction: increasing the hydrogen content or decreasing the oxygen content of an organic molecule).

而氧化反應(oxidation)則正好相反，即有機分子在氧化劑(oxidizing reagent)的作用下發生氫原子減少或氧原子數增加或氧原子數減少的反應。(increasing the oxygen content or decreasing the hydrogen content of an organic molecule)

Oxygen content decreases

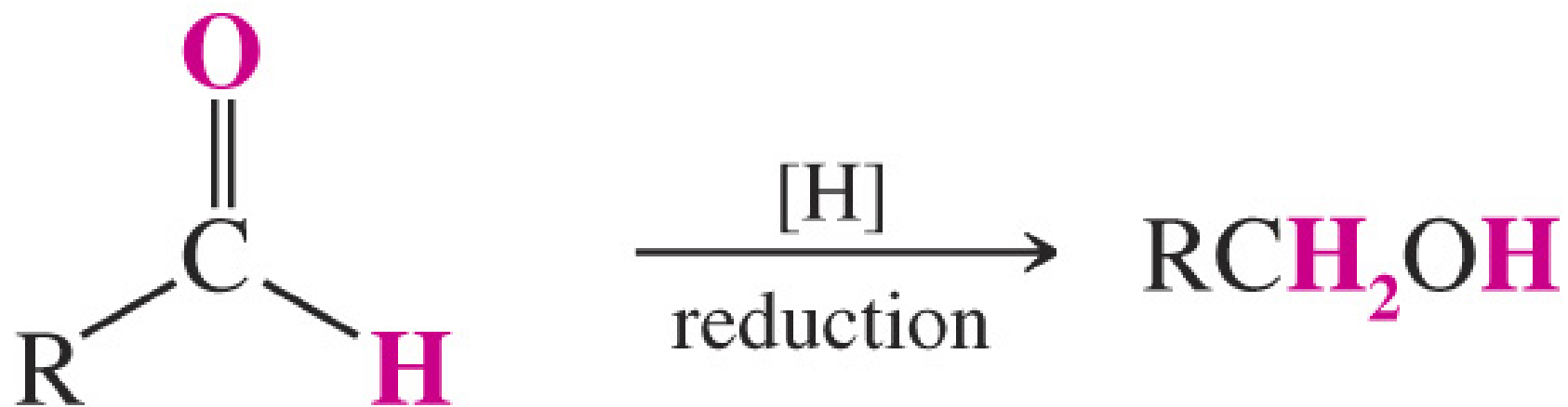


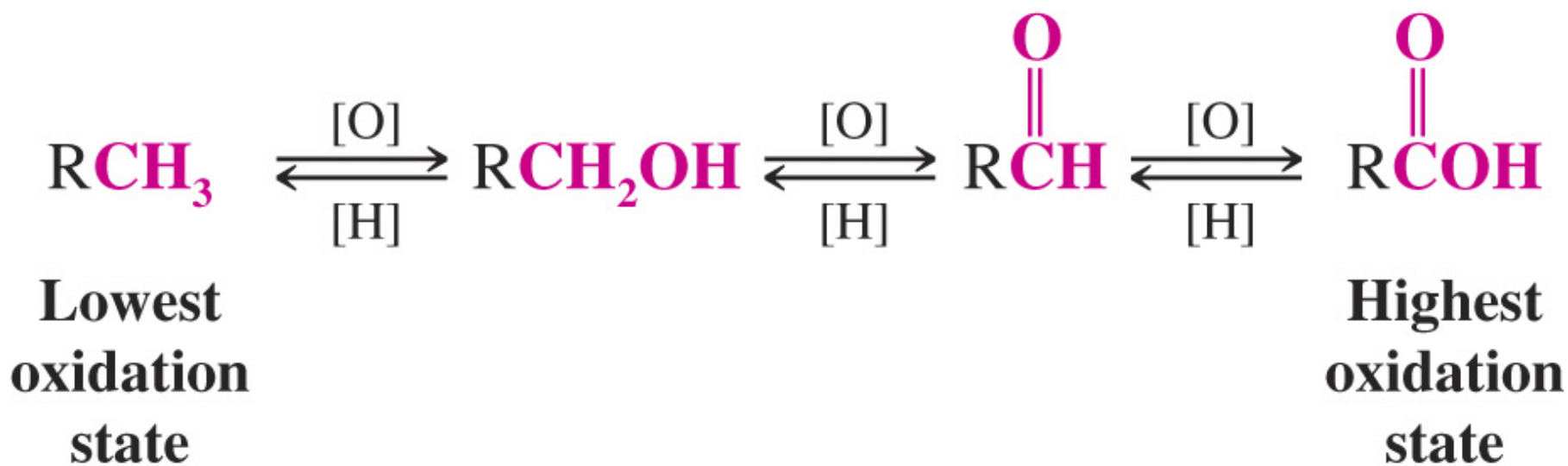
**Carboxylic
acid**



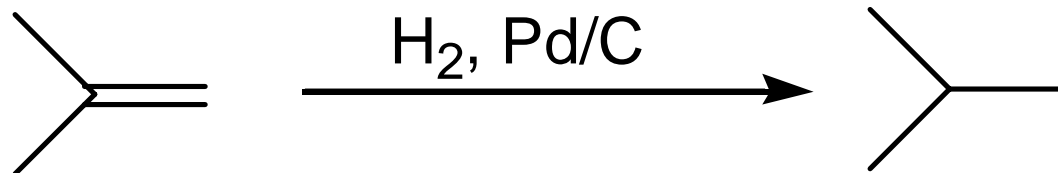
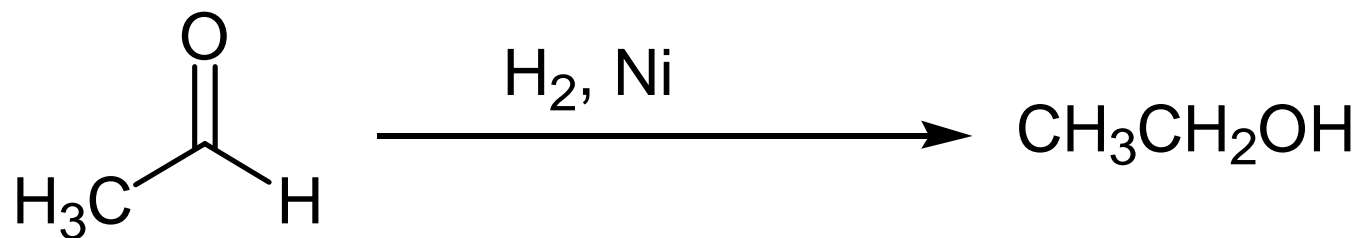
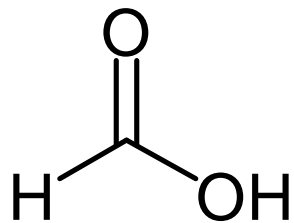
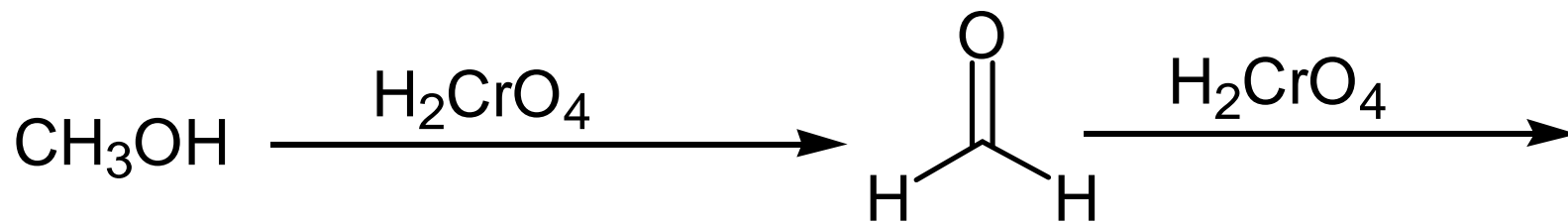
Aldehyde

Hydrogen content increases

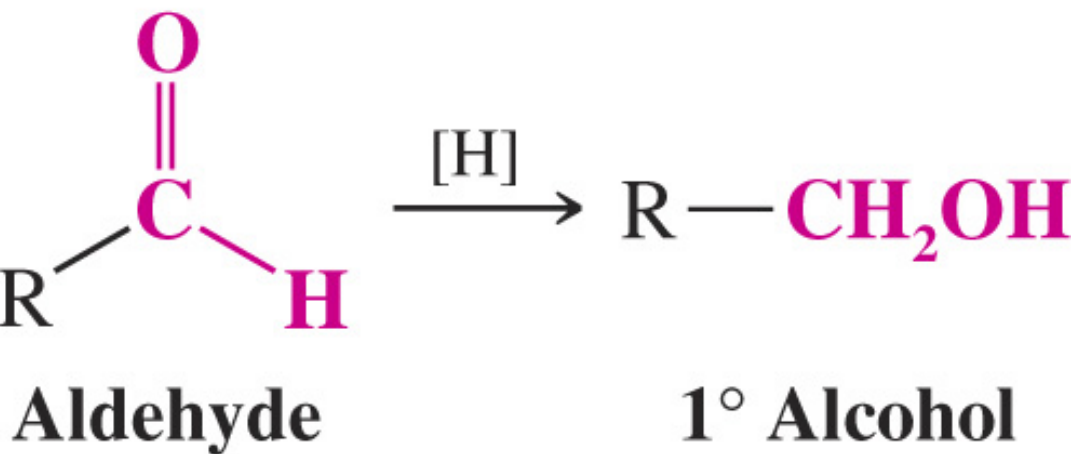
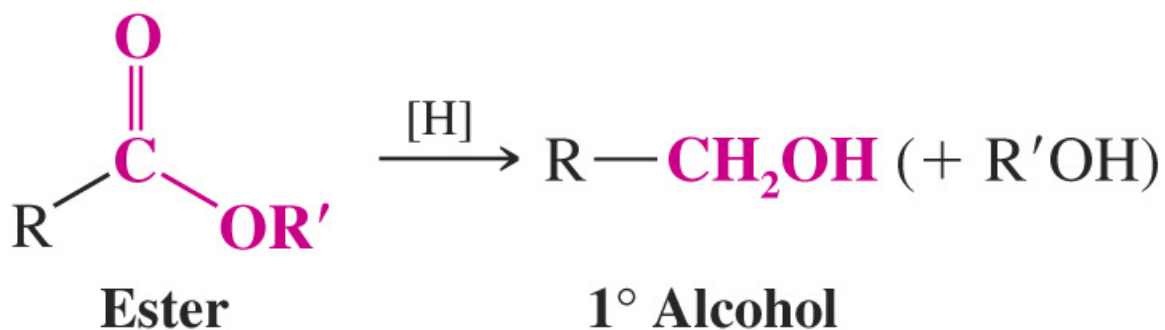
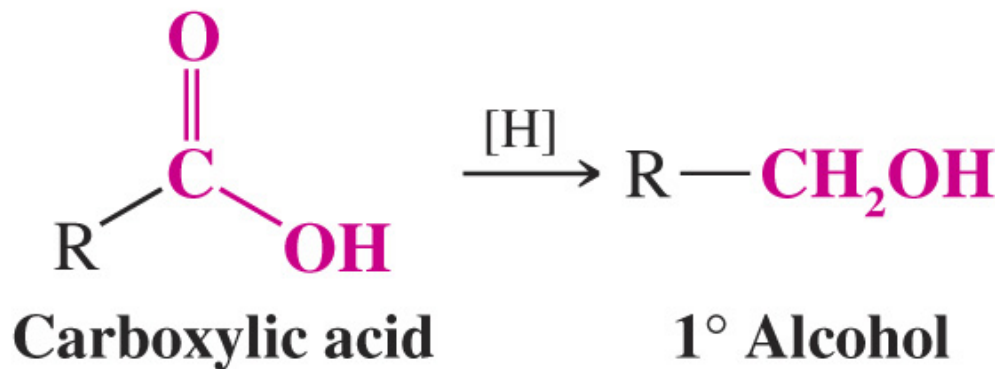


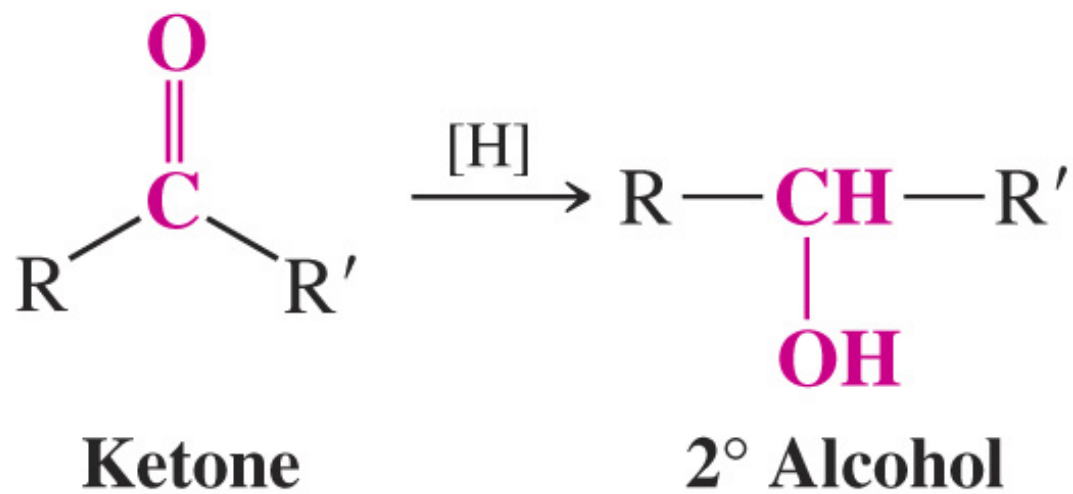


課堂練習 page541 判斷下列反應是還原還是氧化

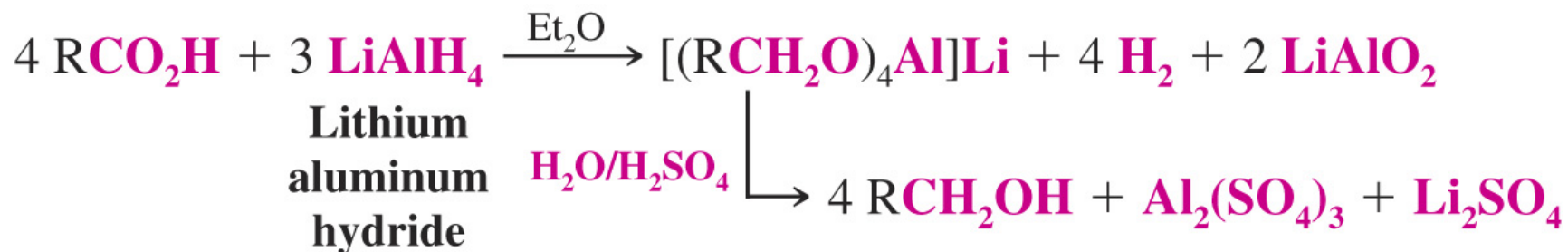


C) carbonyl 化合物的還原反應:

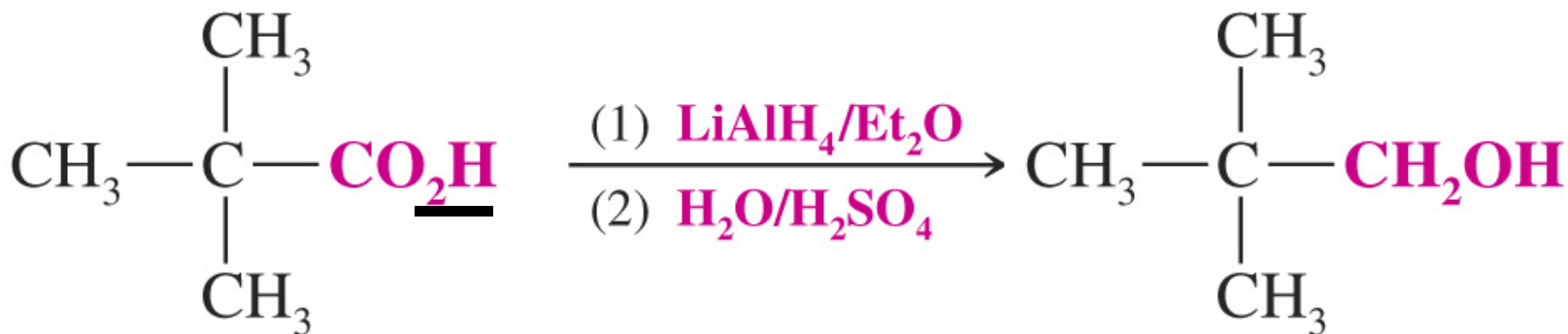
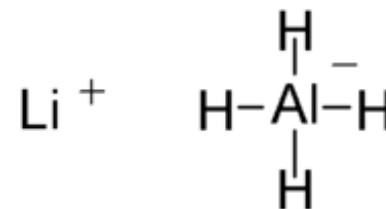




在上述的四種化合物中，carboxylic acid最難被還原，故需用有極強還原能力的lithium aluminum hydride (LiAlH₄)

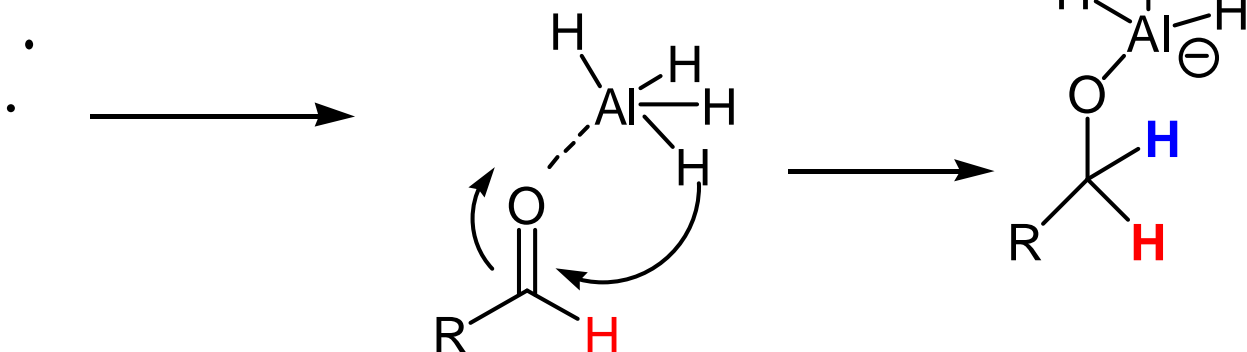
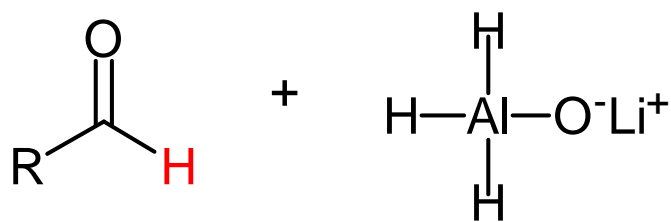
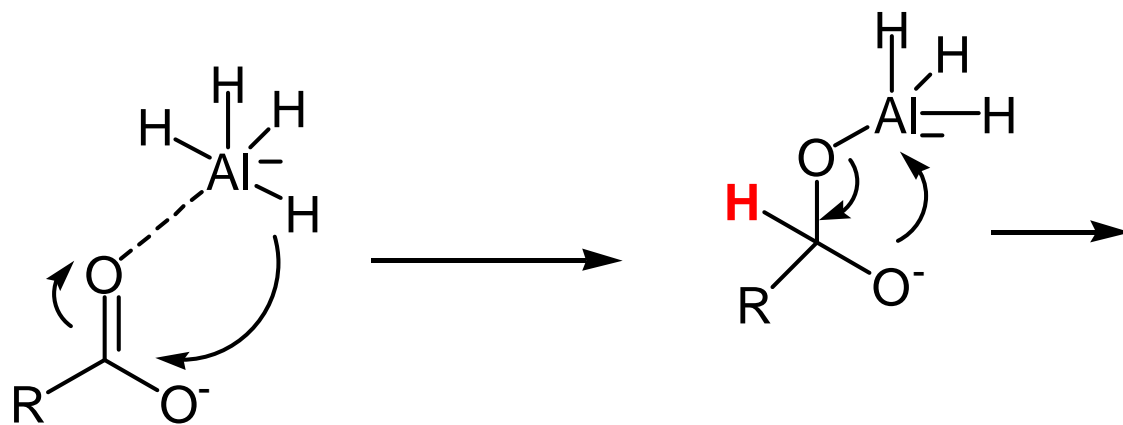
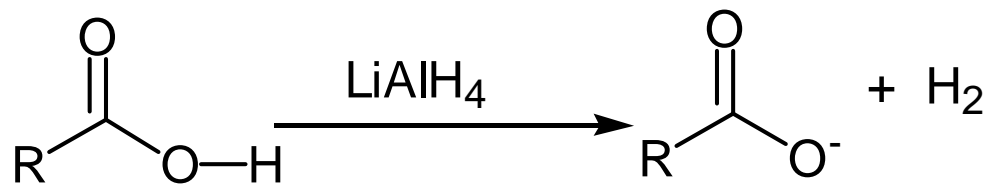


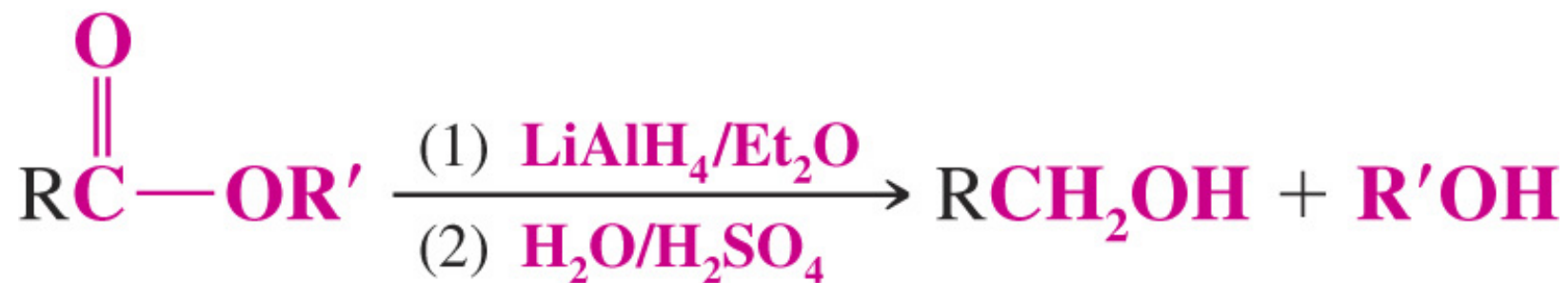
簡略解釋反應機制



2,2-Dimethylpropanoic acid

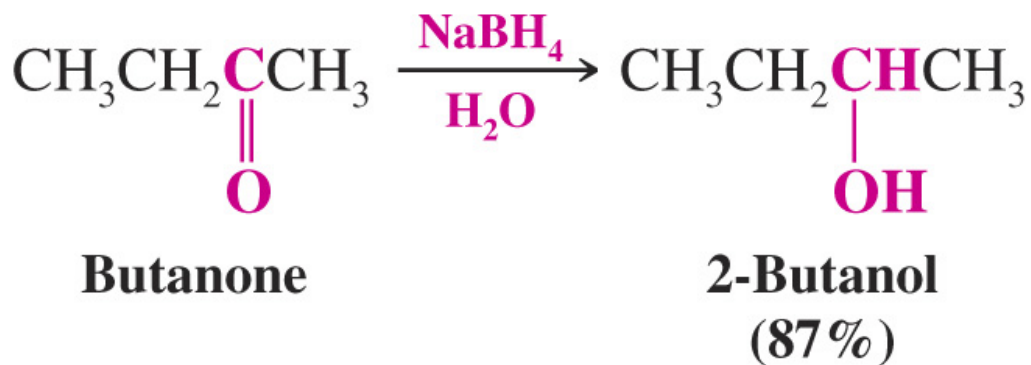
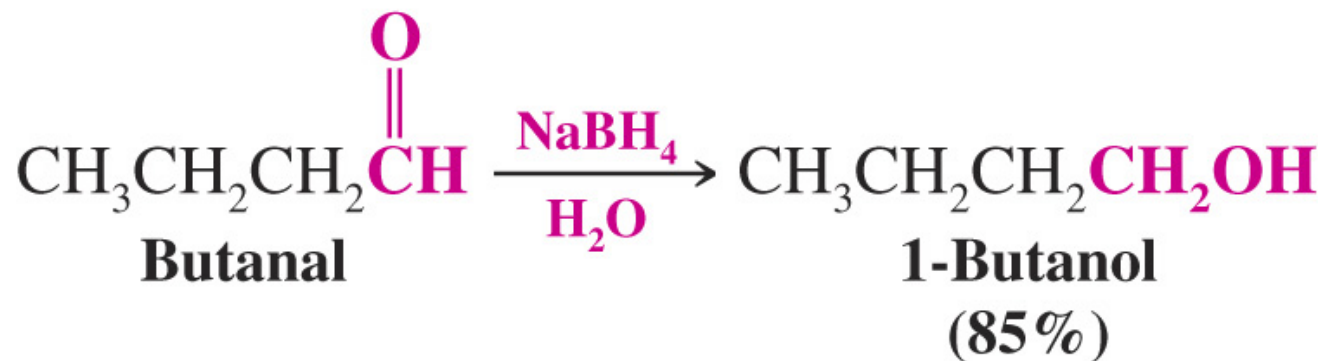
**Neopentyl alcohol
(92%)**

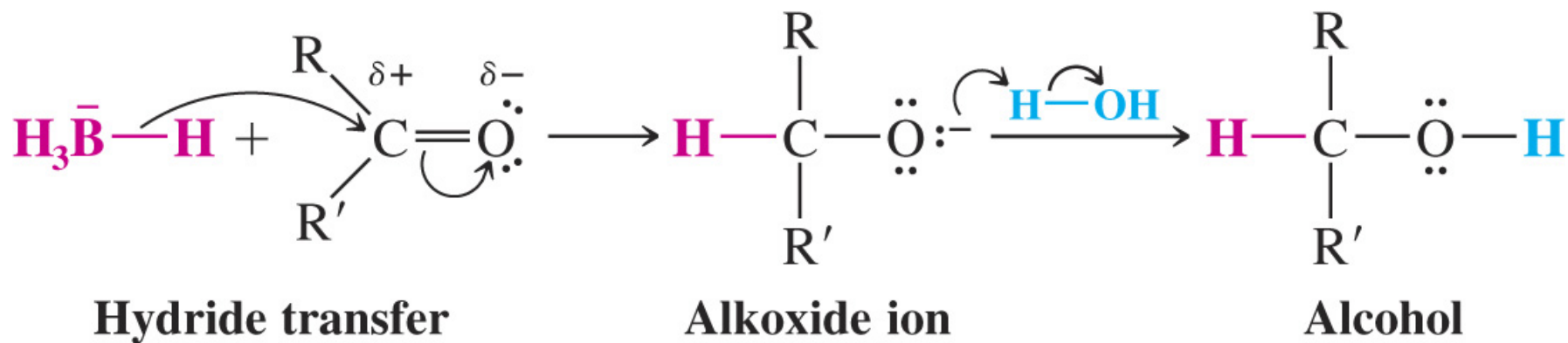




解釋上述反應機制

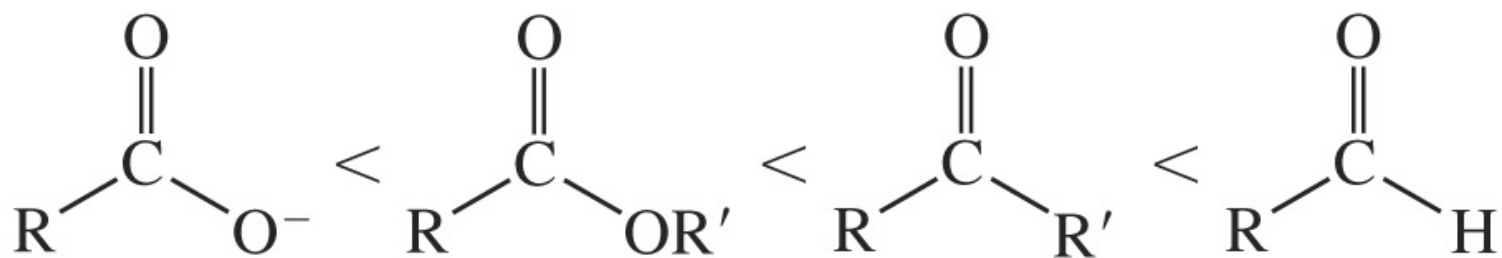
與酸和酯相比較，醛和酮較容易被還原，故可用sodium borohydride (NaBH₄)





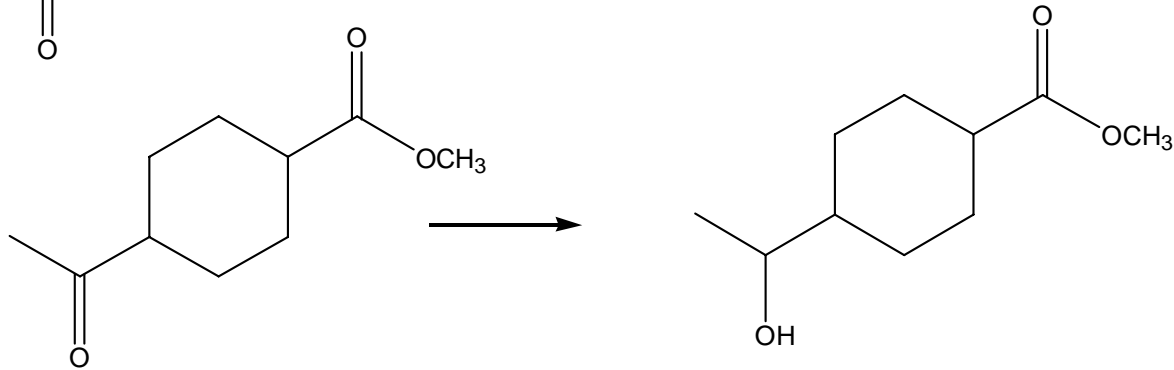
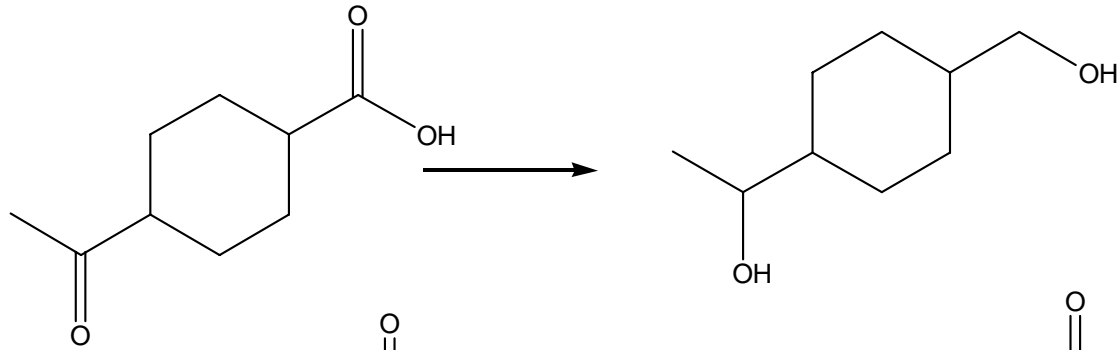
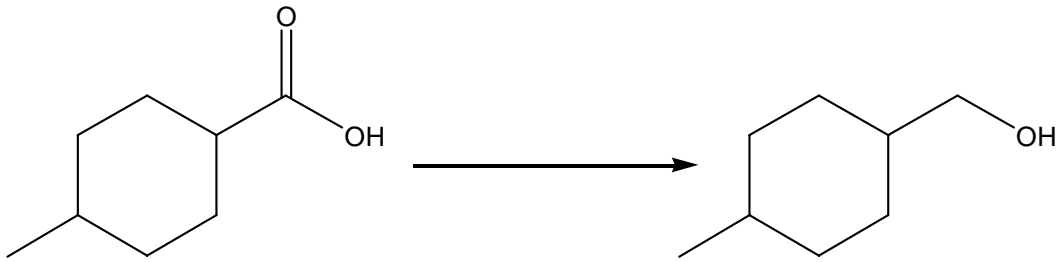
Reduced by LiAlH_4

Reduced by NaBH_4

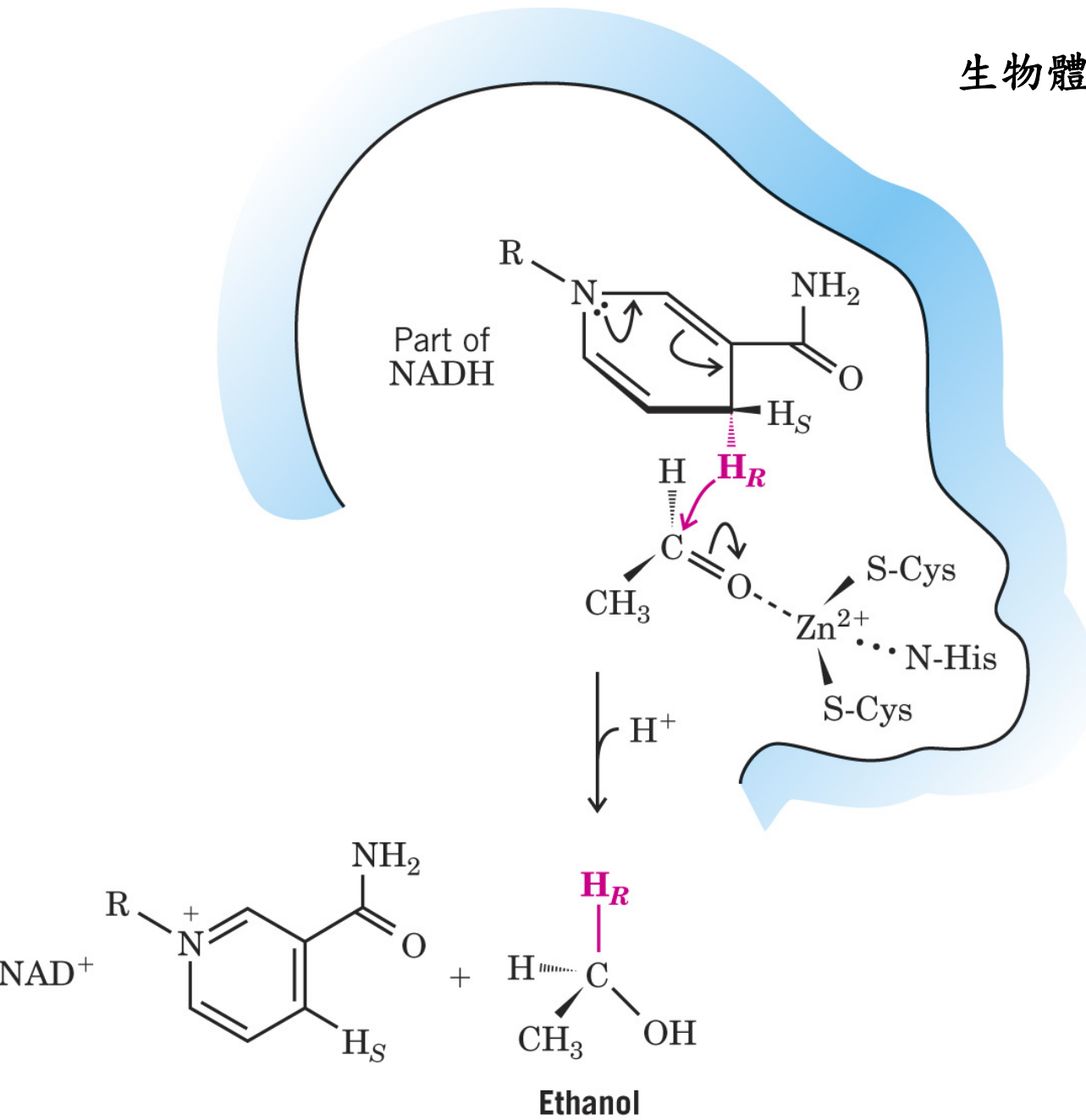


Ease of reduction

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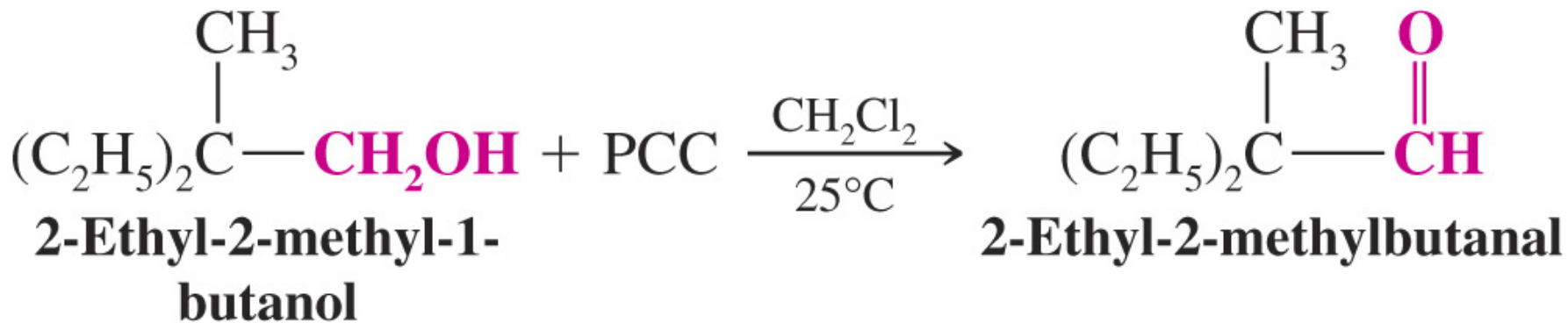
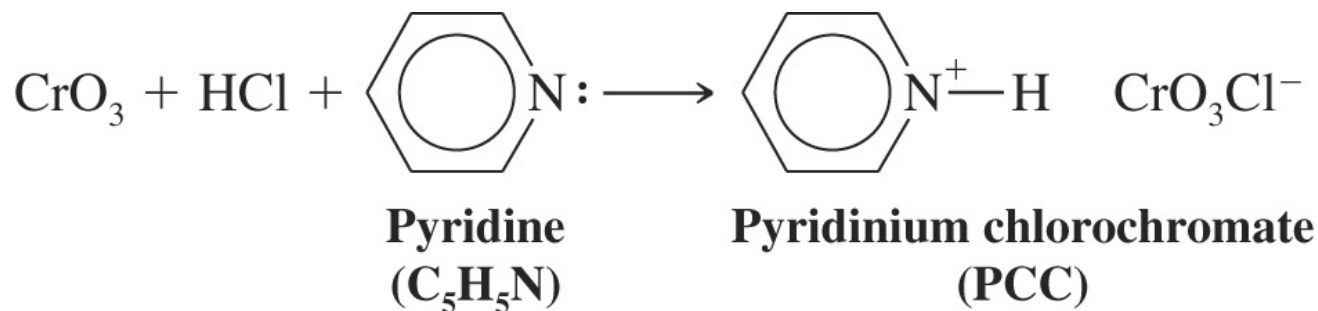


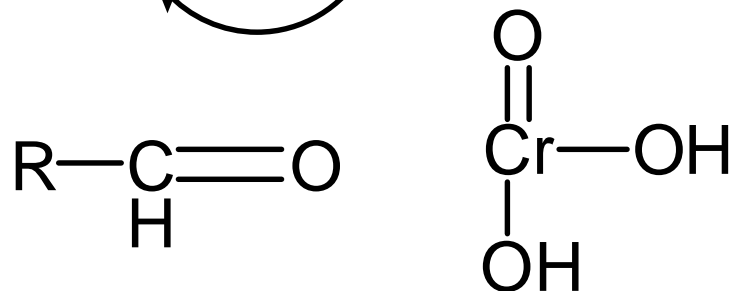
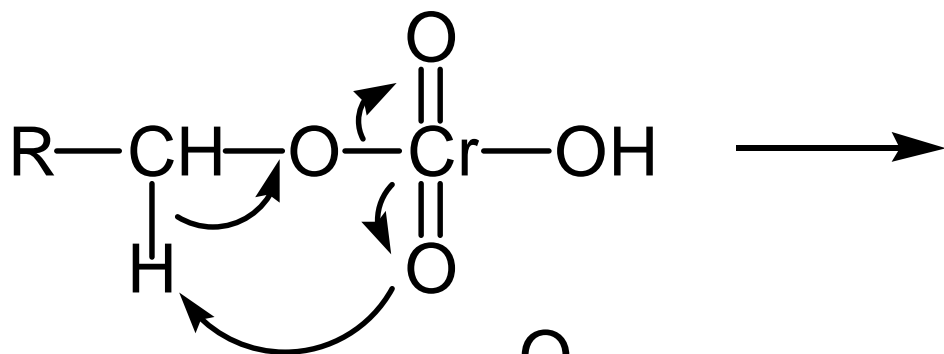
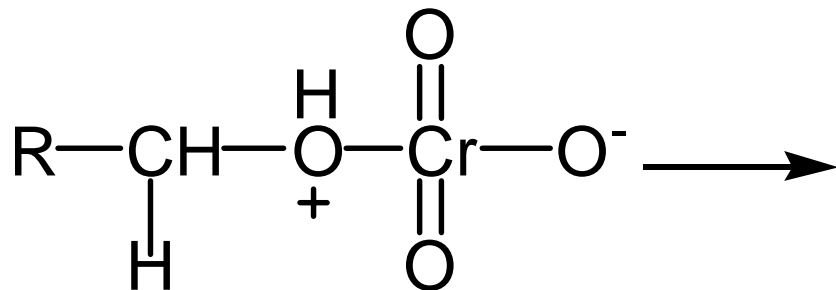
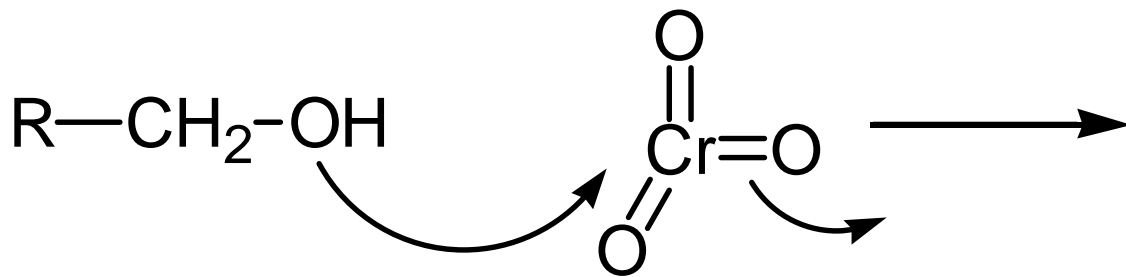
生物體內的立體選擇性還原



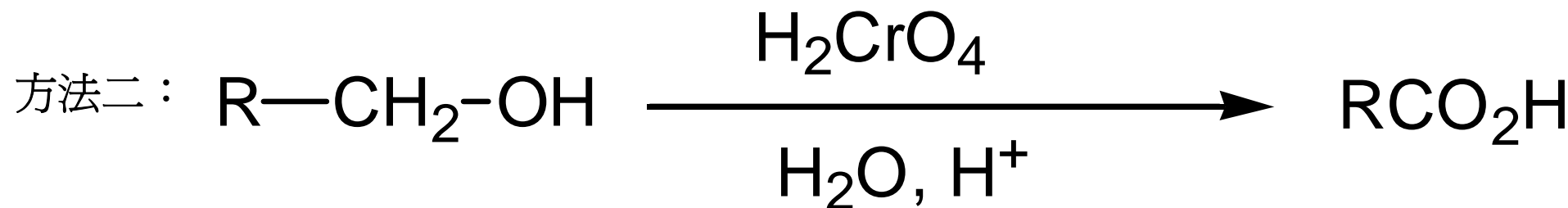
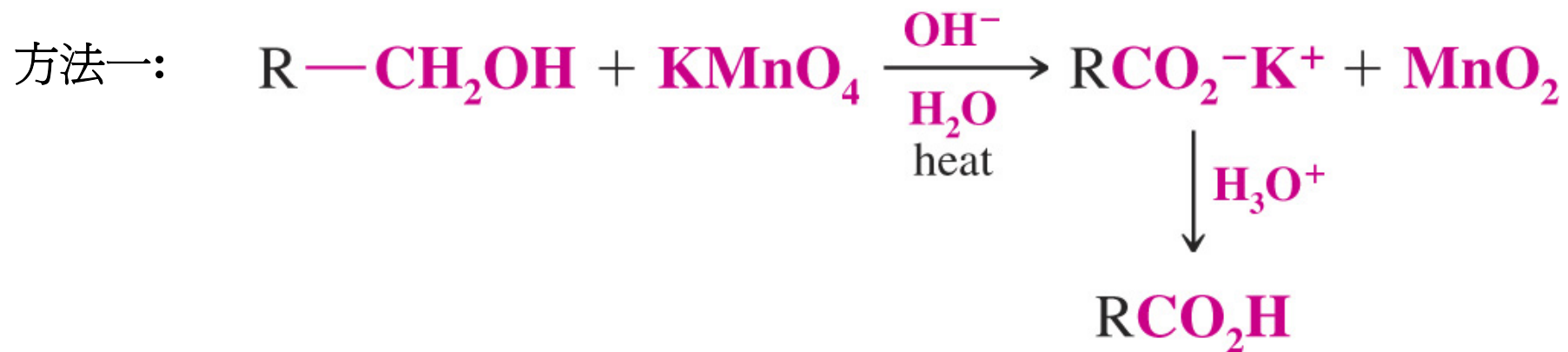
2) 將醇氧化成酮, 醛或酸:

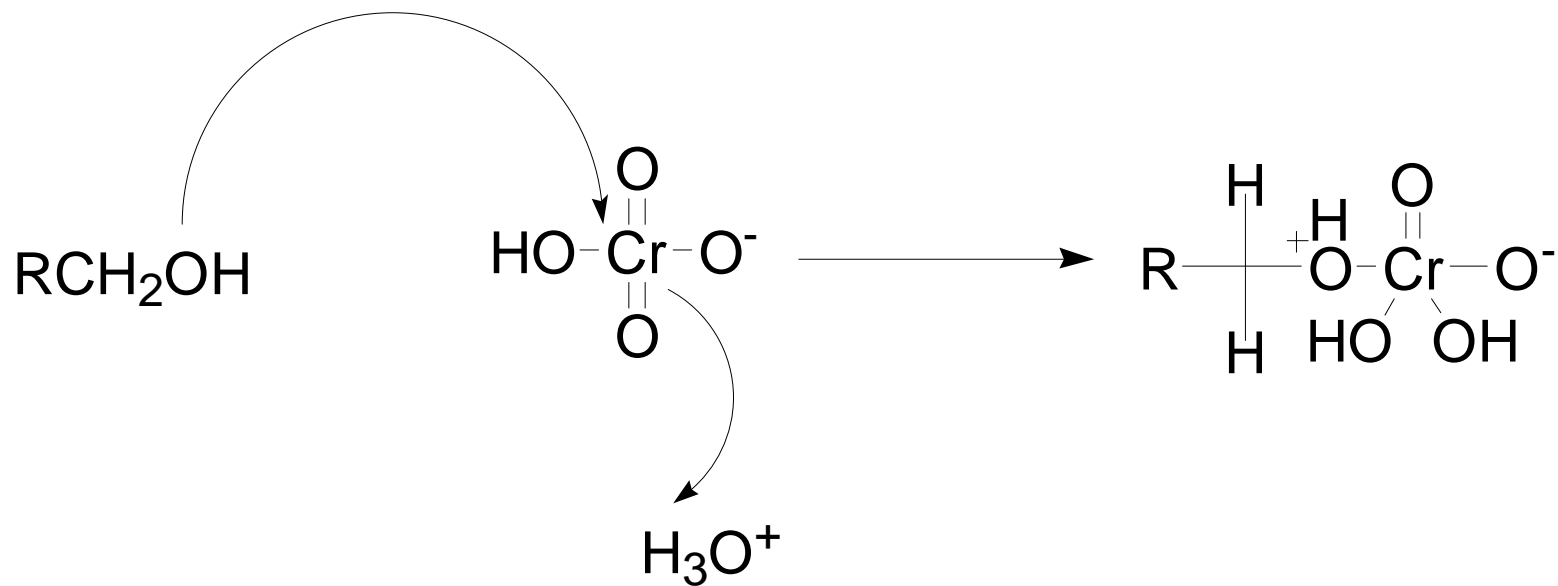
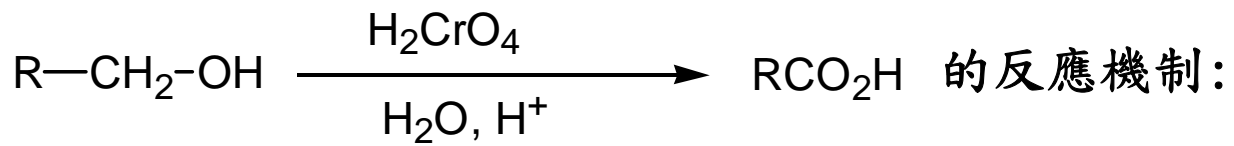
a) 將一級醇氧化成醛: pyridinium chlorochromate (PCC)

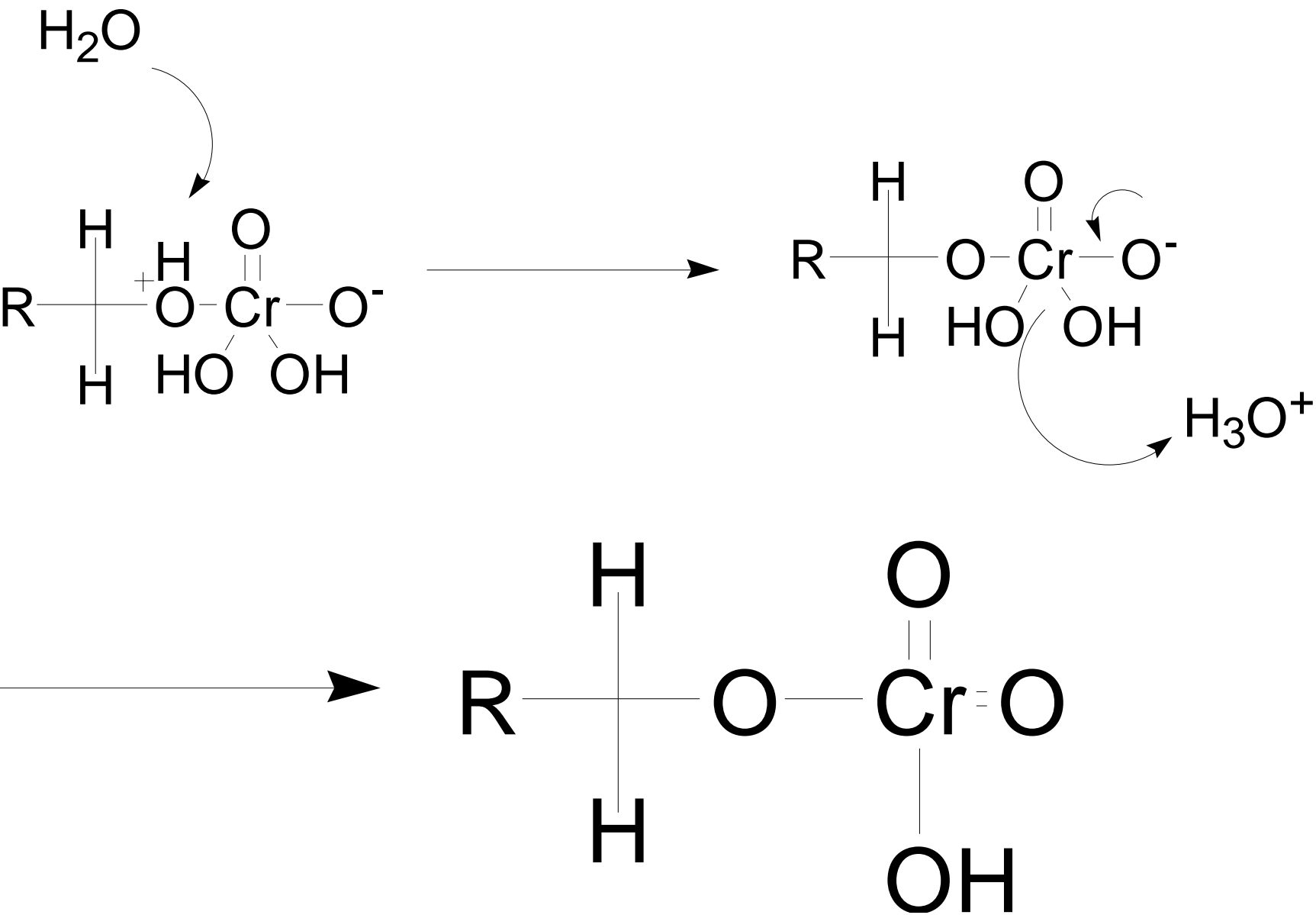


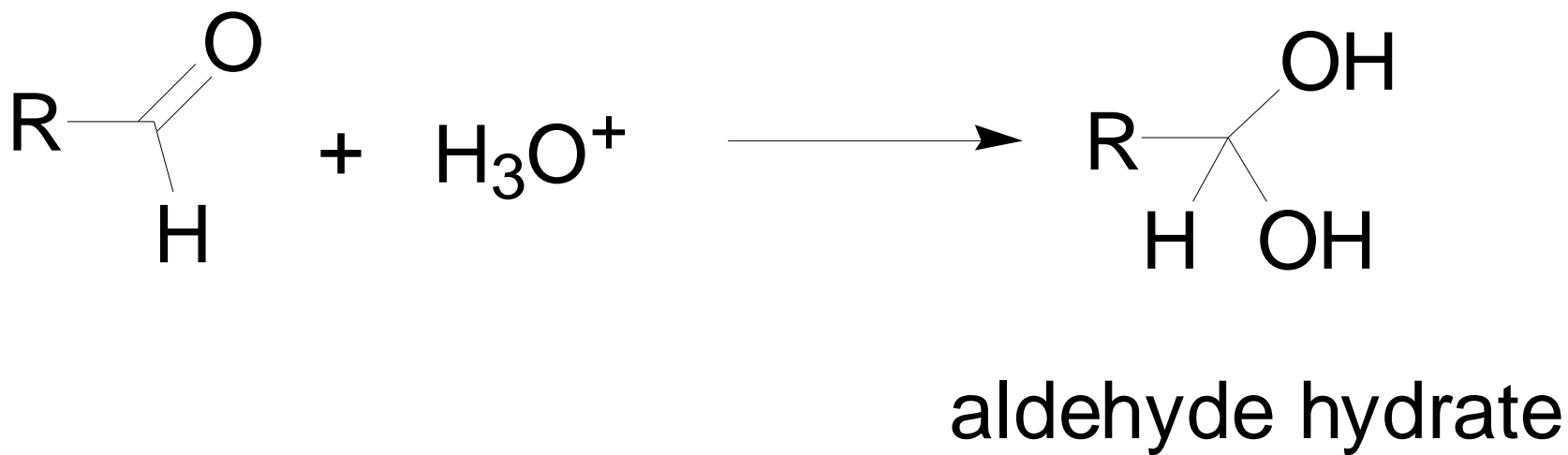


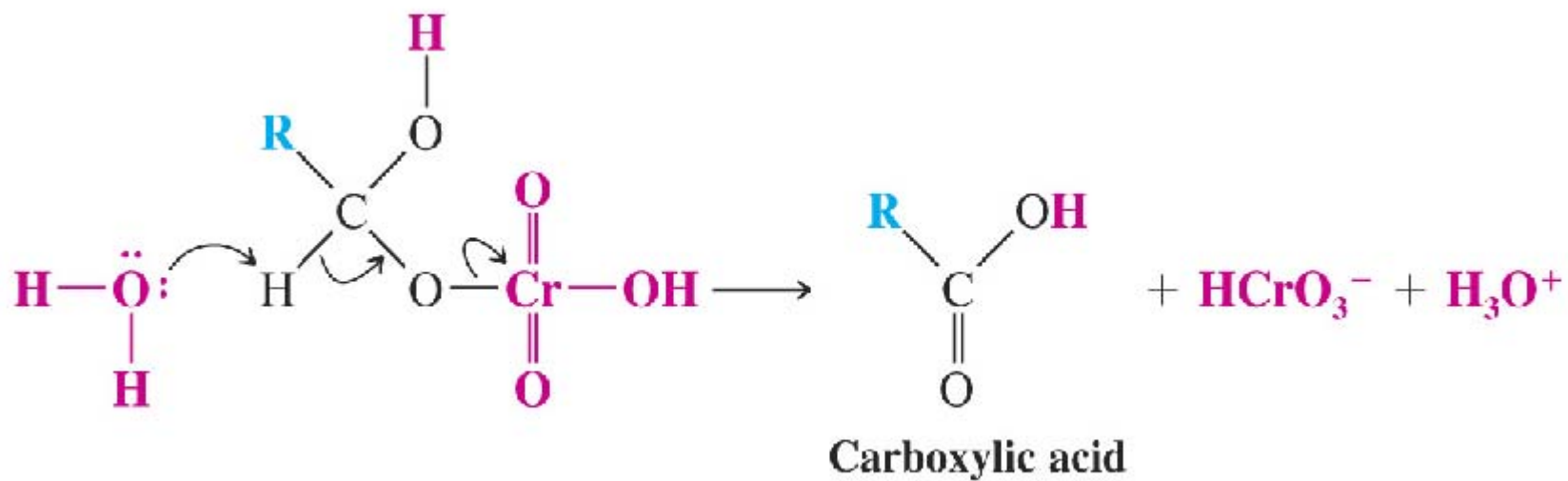
b) 將一級醇氧化成酸：



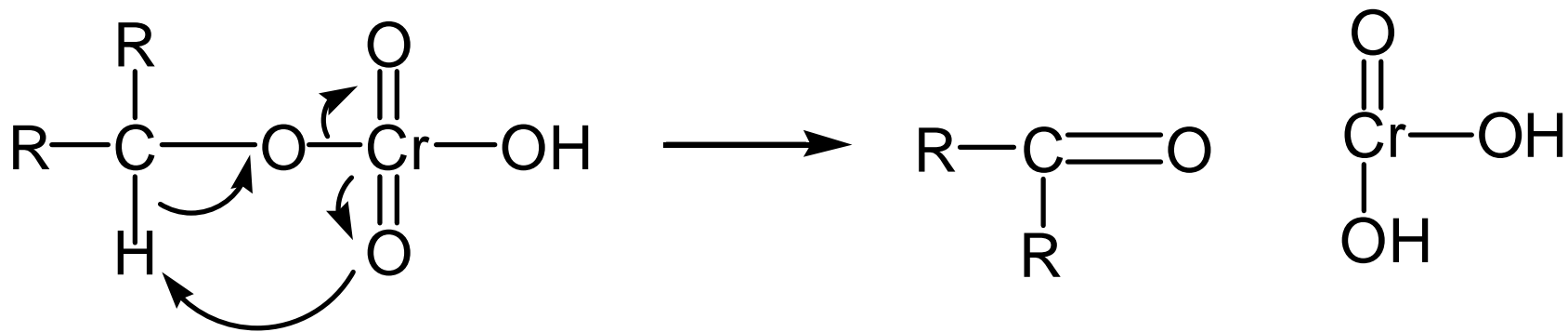
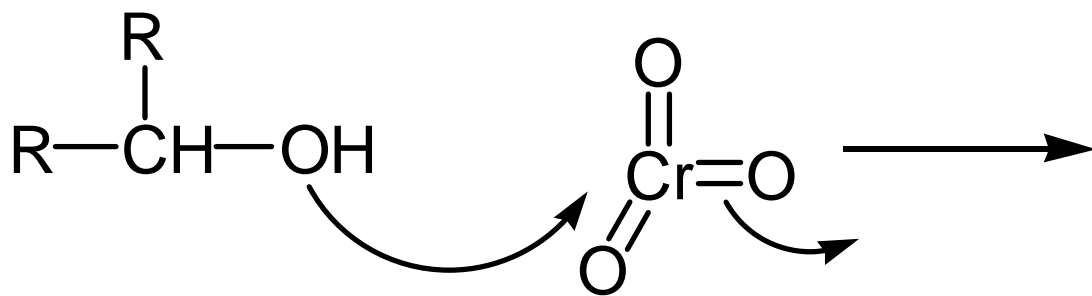
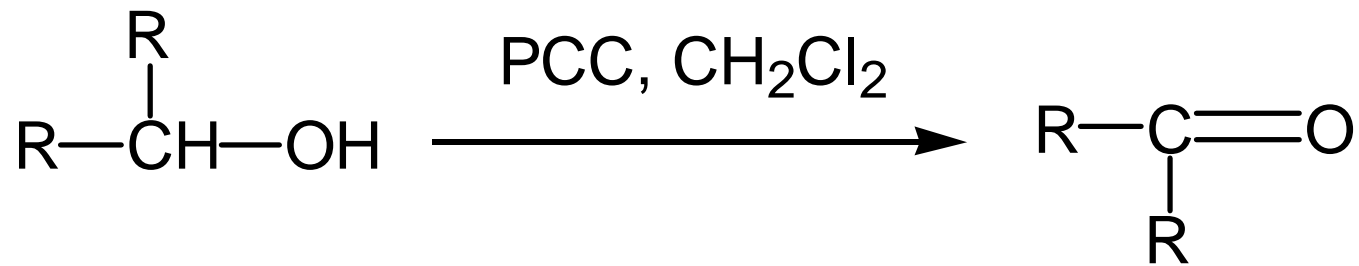


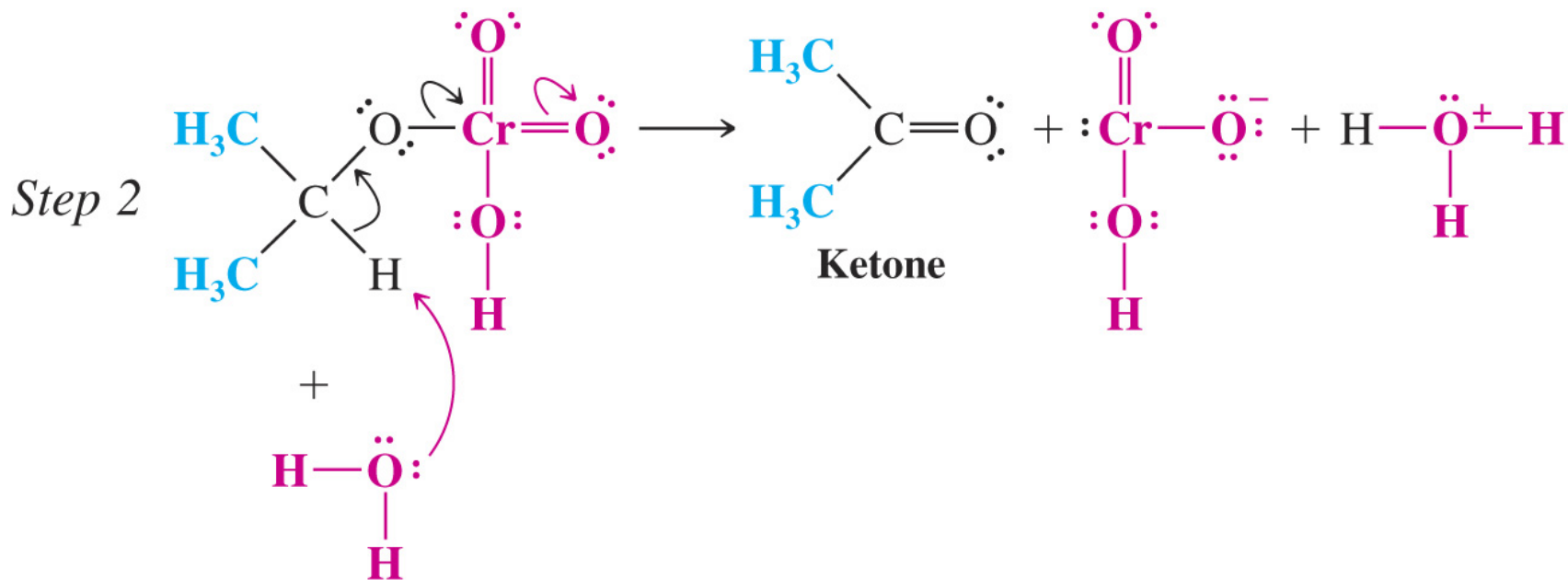
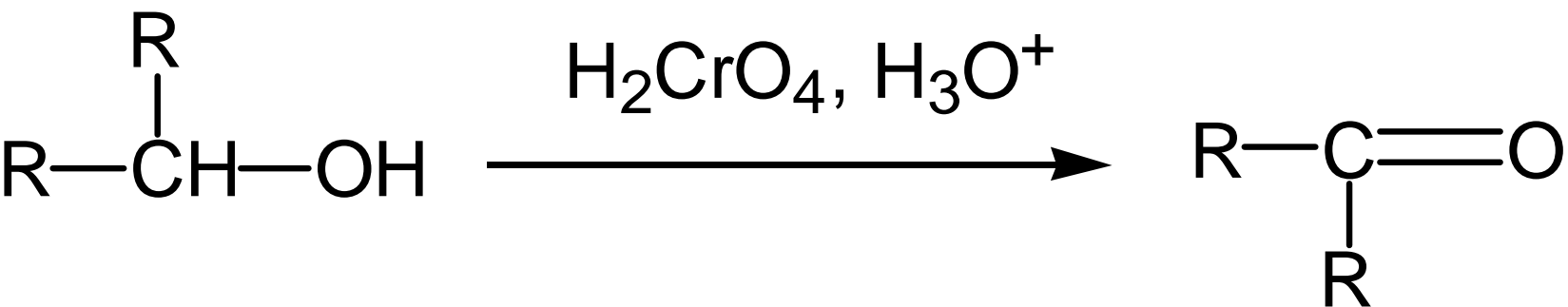






b) 將二級醇氧化成酮:

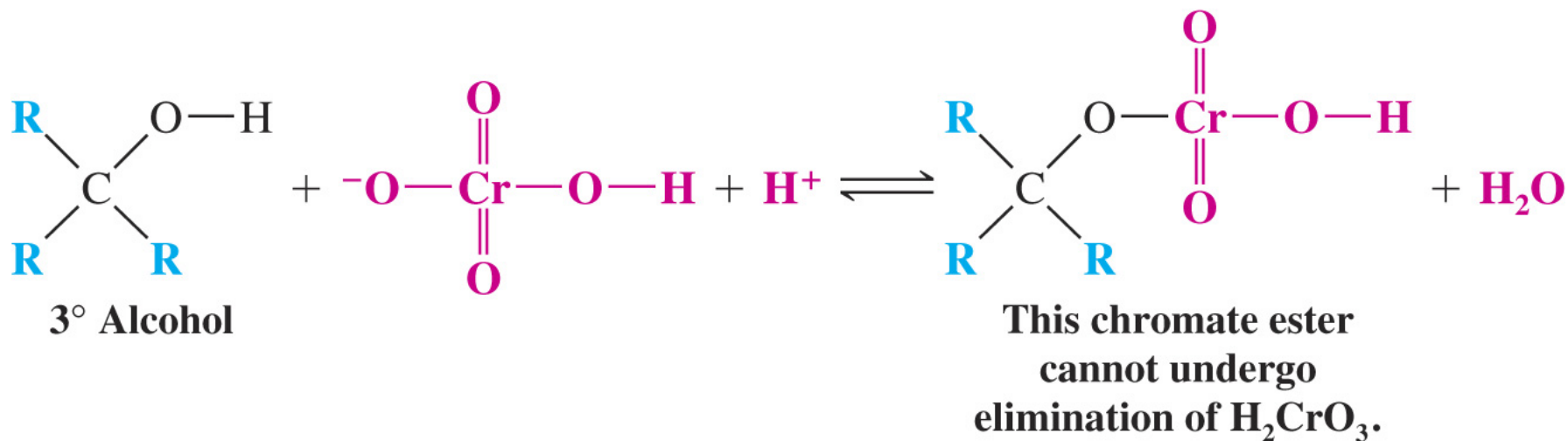




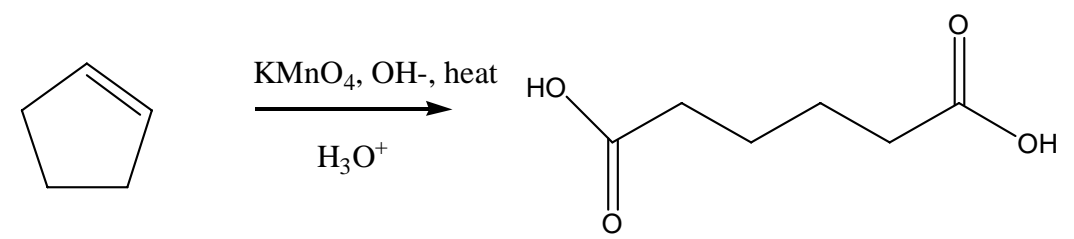
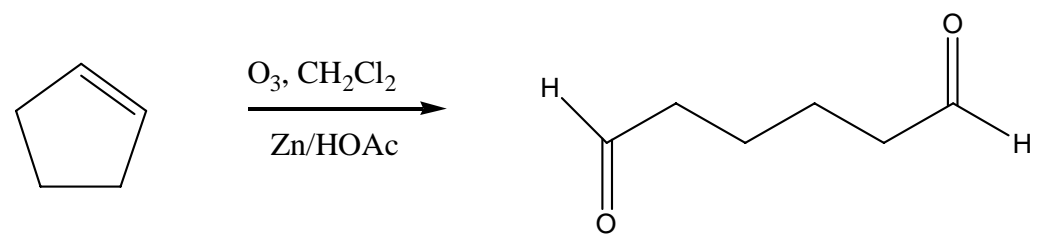
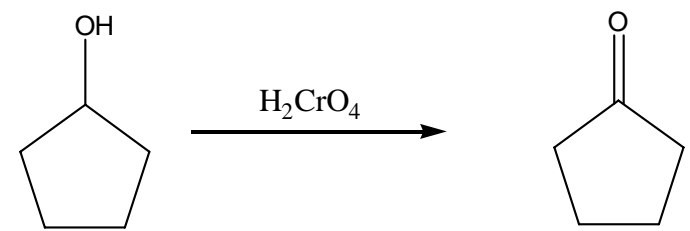
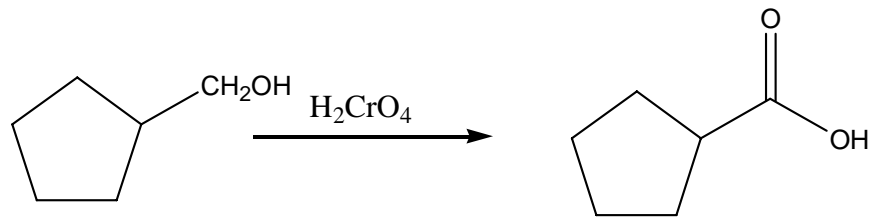
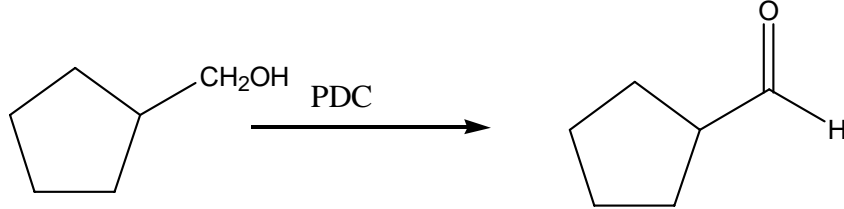
The chromium atom departs with a pair of electrons that formerly belonged to the alcohol; the alcohol is thereby oxidized and the chromium reduced.

故我們可得出：

- 1) 一級醇用PCC氧化可轉化成醛
- 2) 一級醇用H₂CrO₄氧化可轉化成酸
- 3) 二級醇用PCC或H₂CrO₄氧化都可轉化成酮
- 4) 三級醇不能被氧化：



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3) 有機金屬 (organometallic reagents) 試劑:

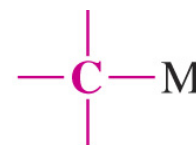
A) 有機金屬試劑的製備:



Primarily ionic
(M = Na⁺ or K⁺)

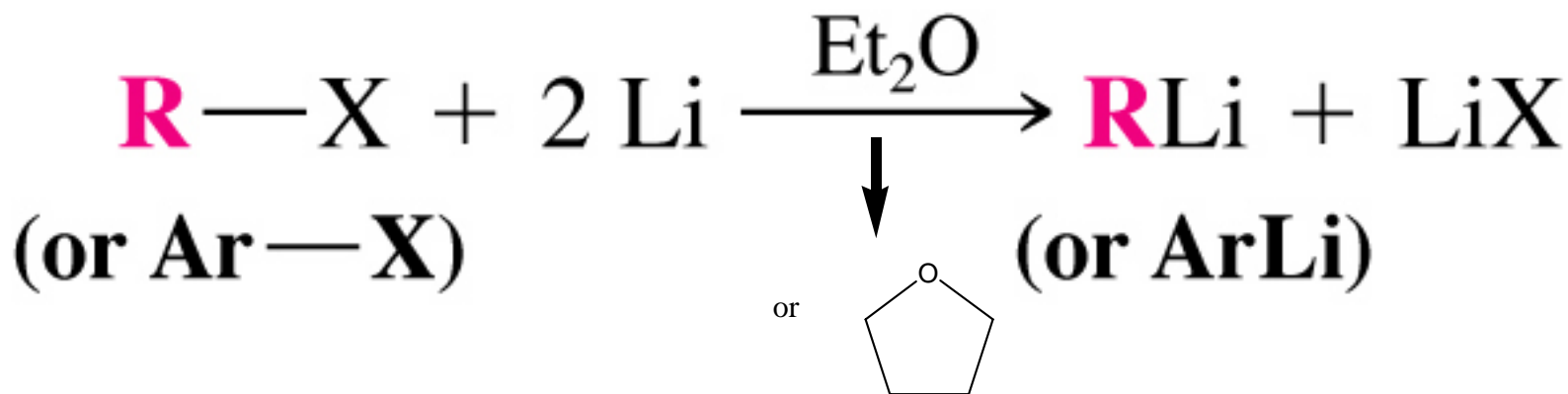


(M = Mg or Li)



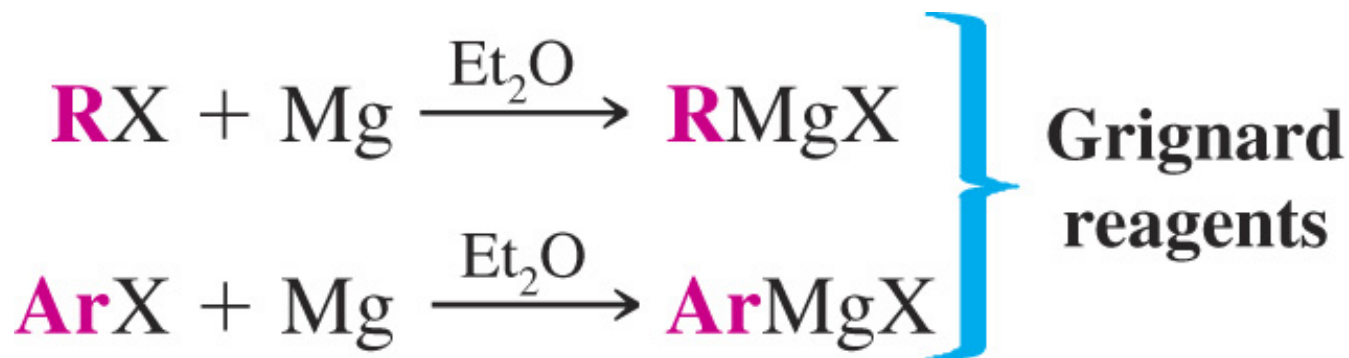
Primarily covalent
(M = Pb, Sn, Hg, or Tl)

a) Organolithium:

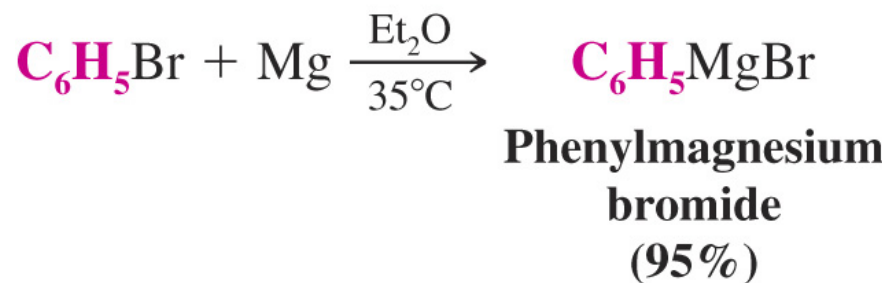
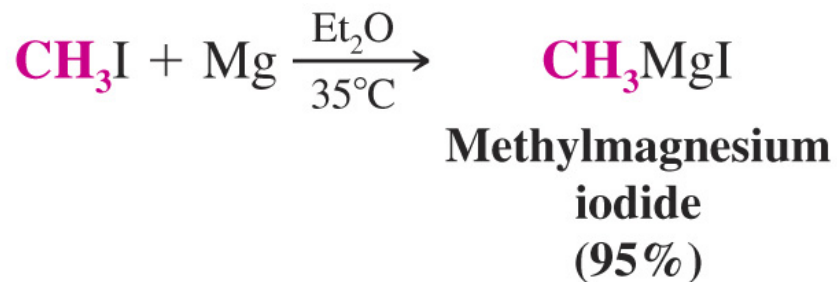


反應活性: R-I > R-Br > R-Cl

b) Grignard reagents:

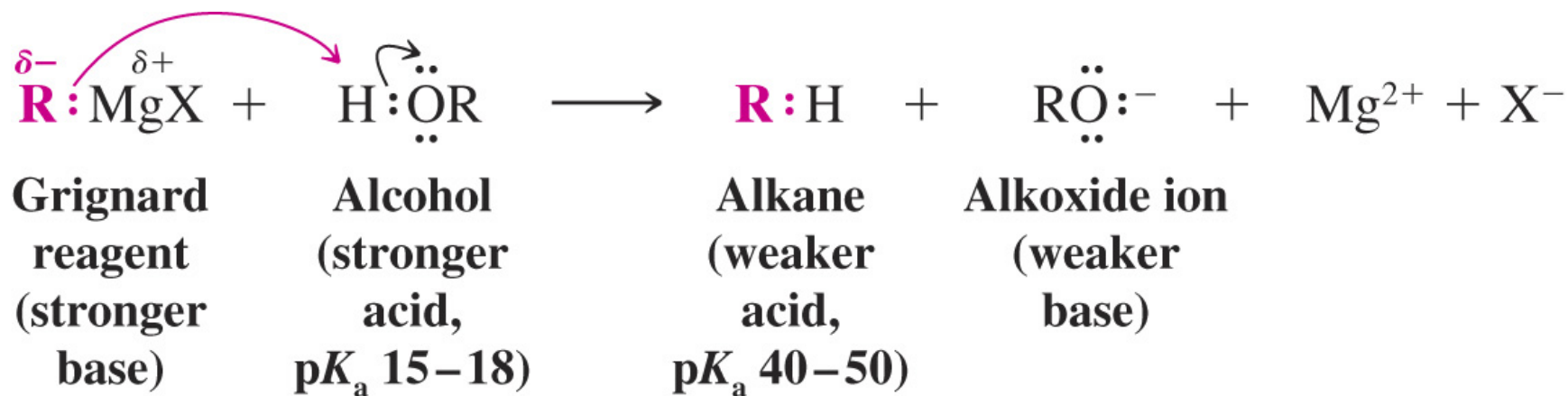
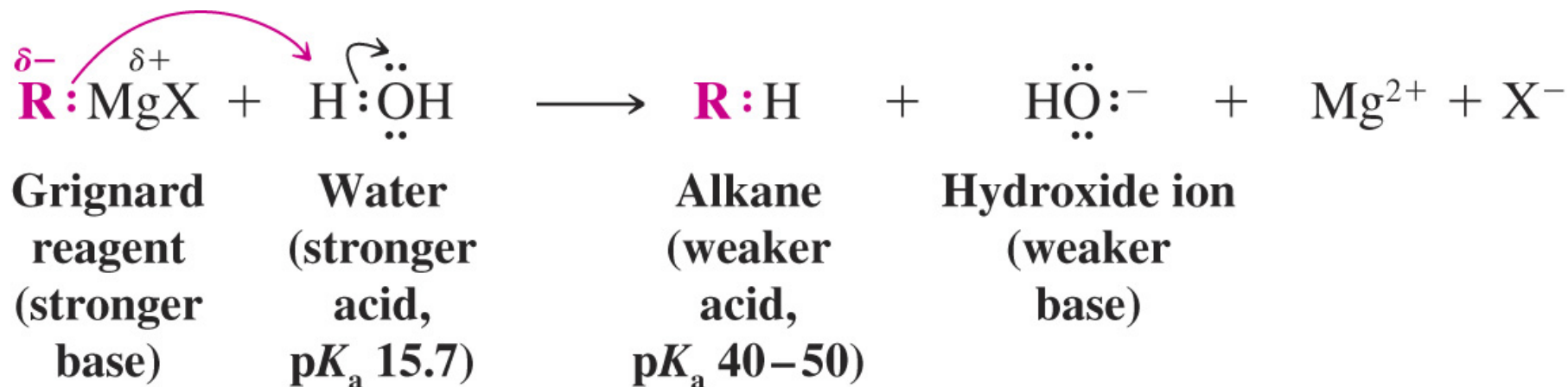


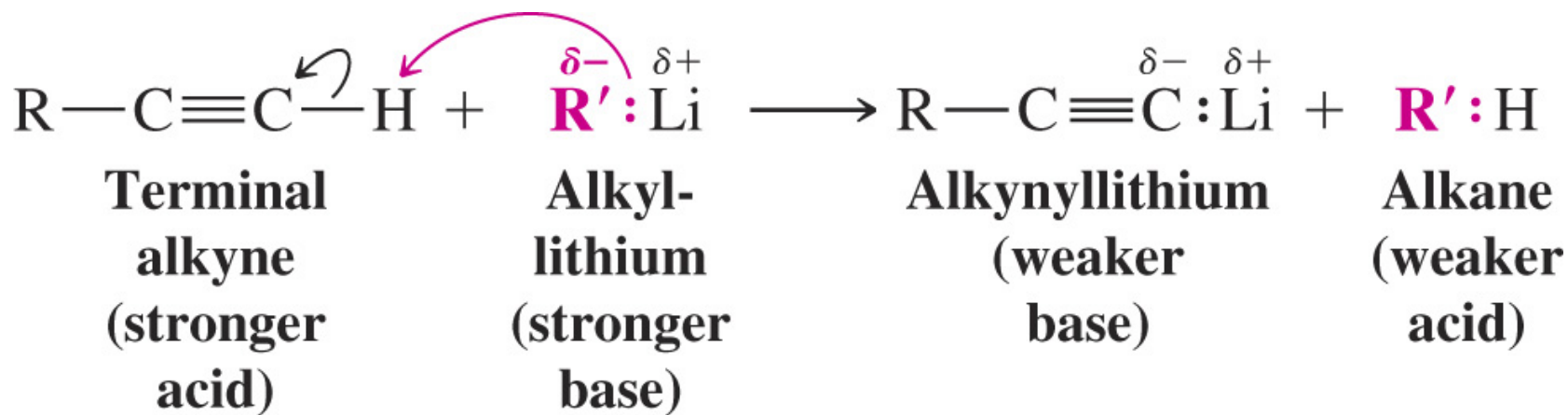
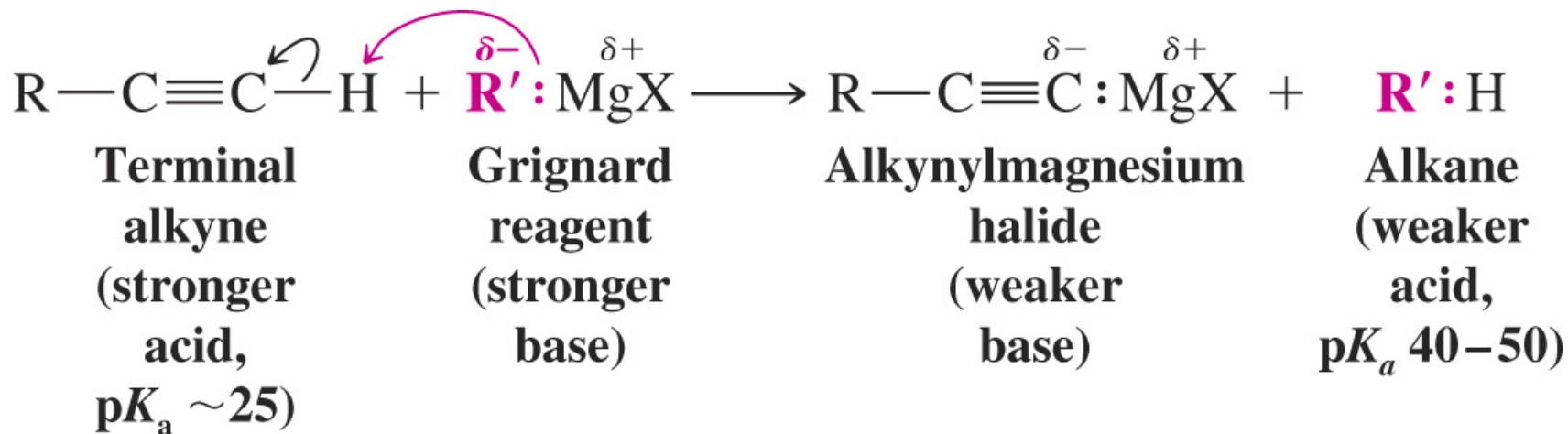
反應活性：R-I > R-Br > R-Cl



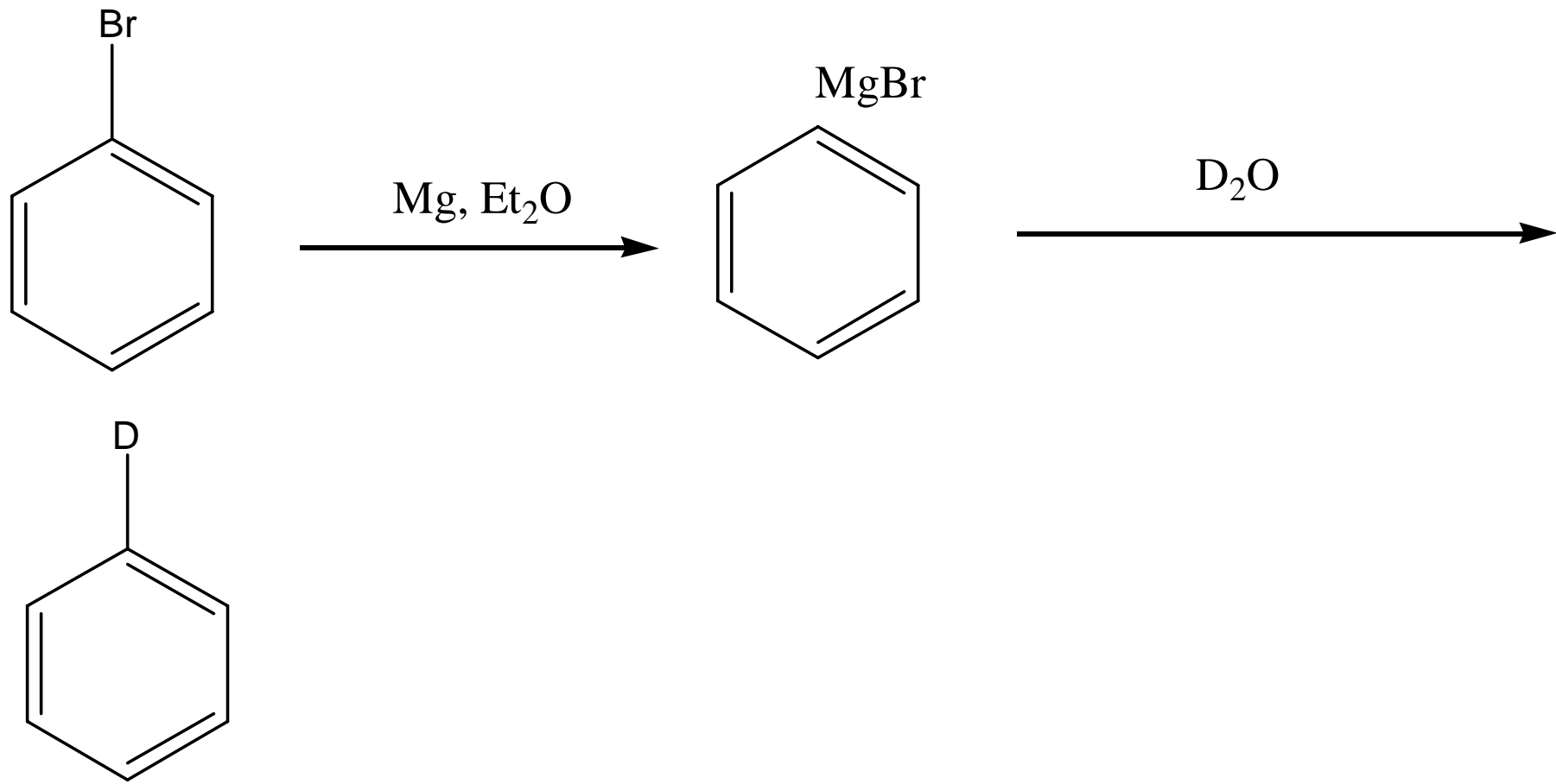
B) Organolithium和Grignard reagents的反應:

a) 酸鹼反應:

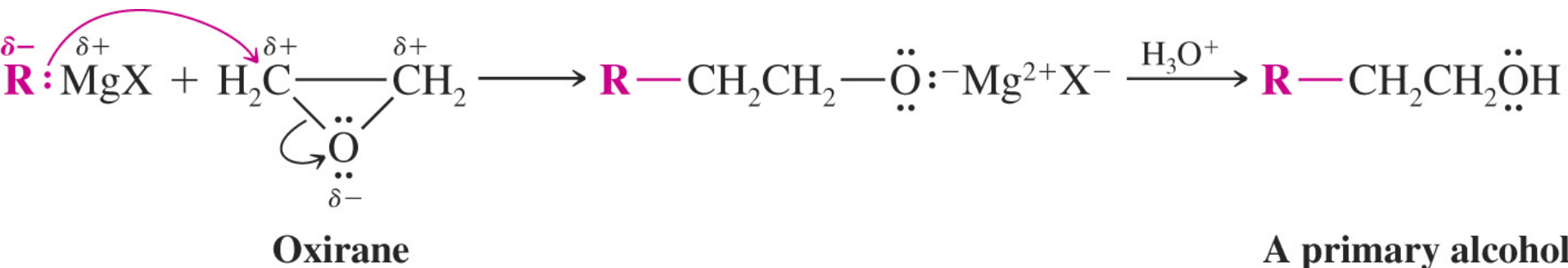




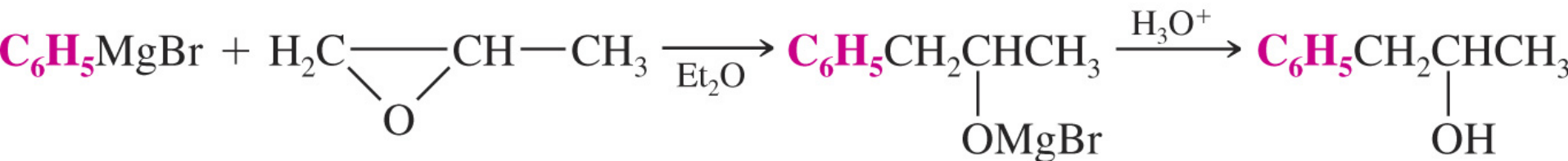
課堂練習 page554 如何由PhBr製備C6H5D



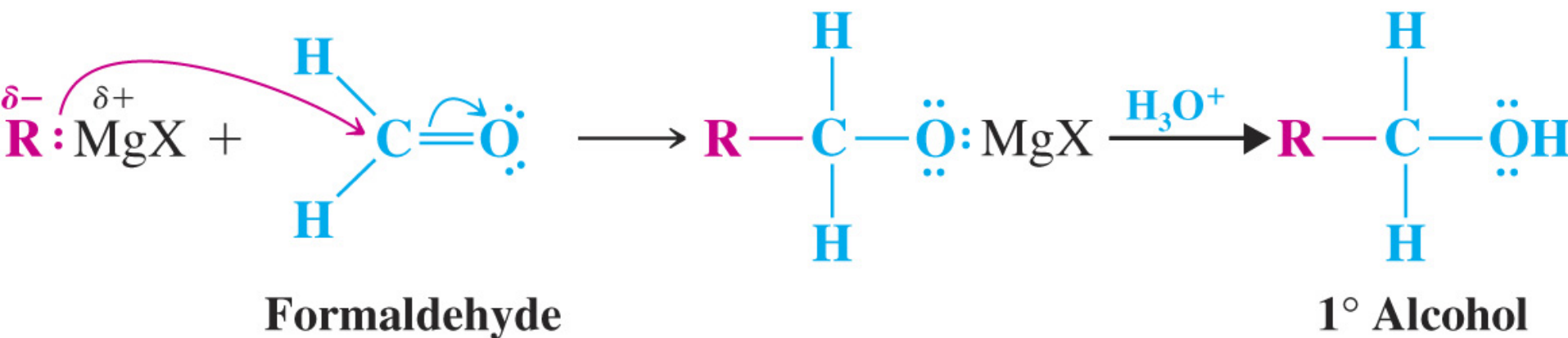
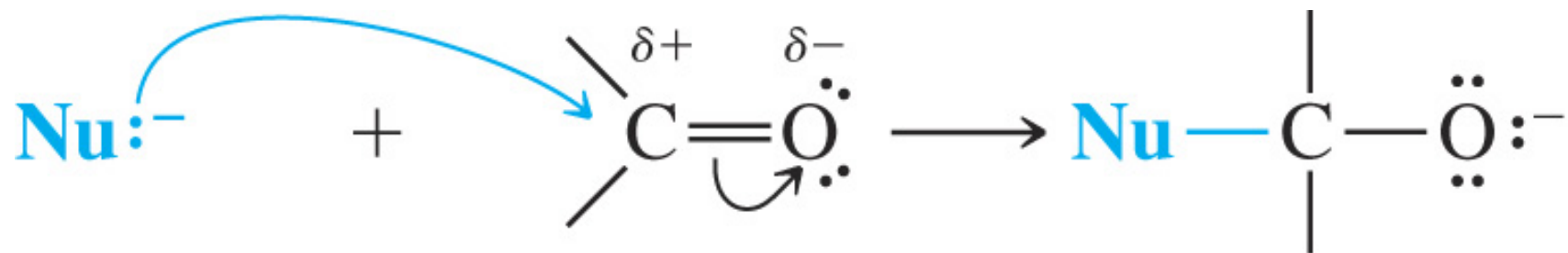
b) Grignard reagents與Oxiranes的反應：

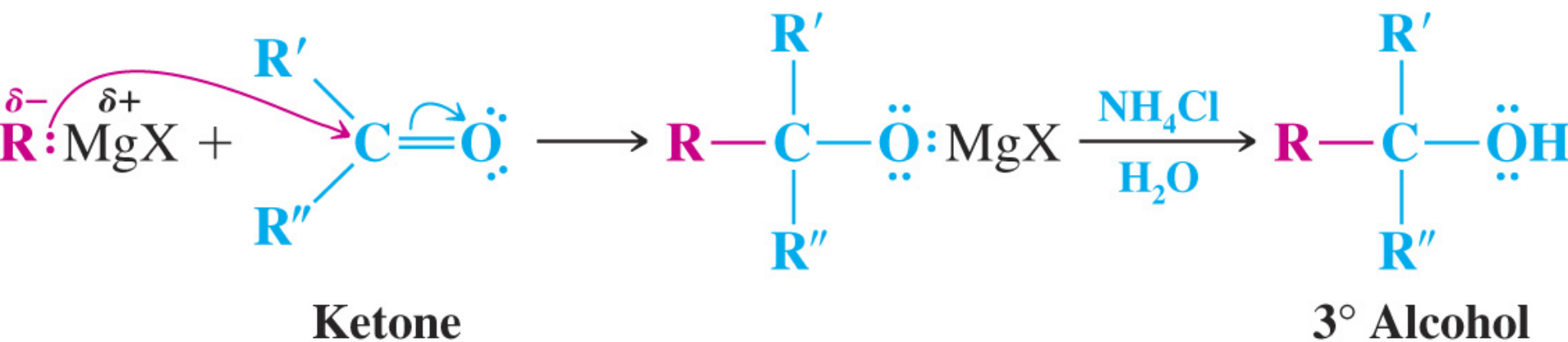
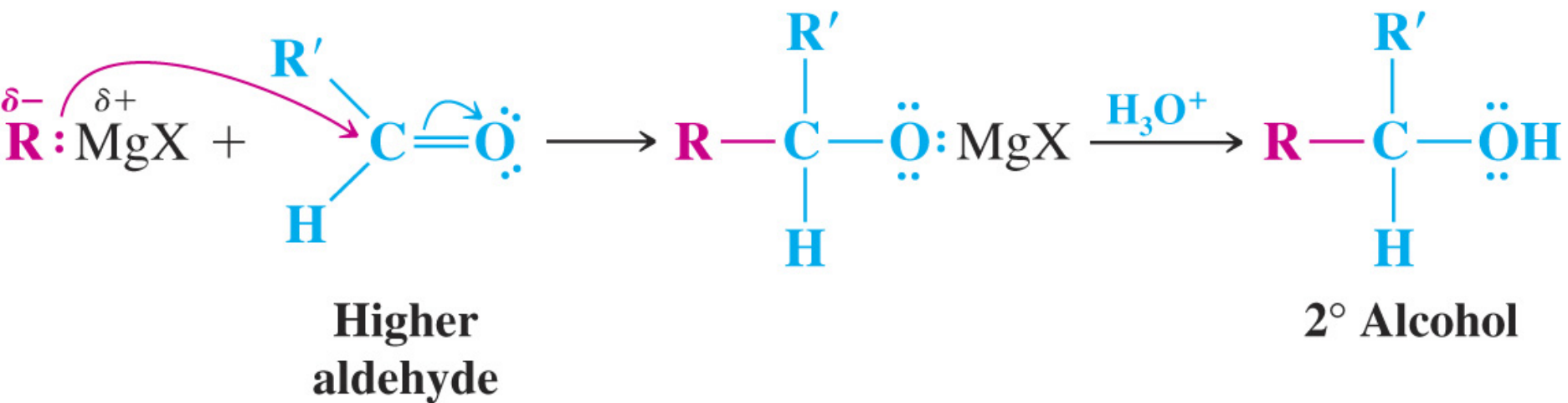


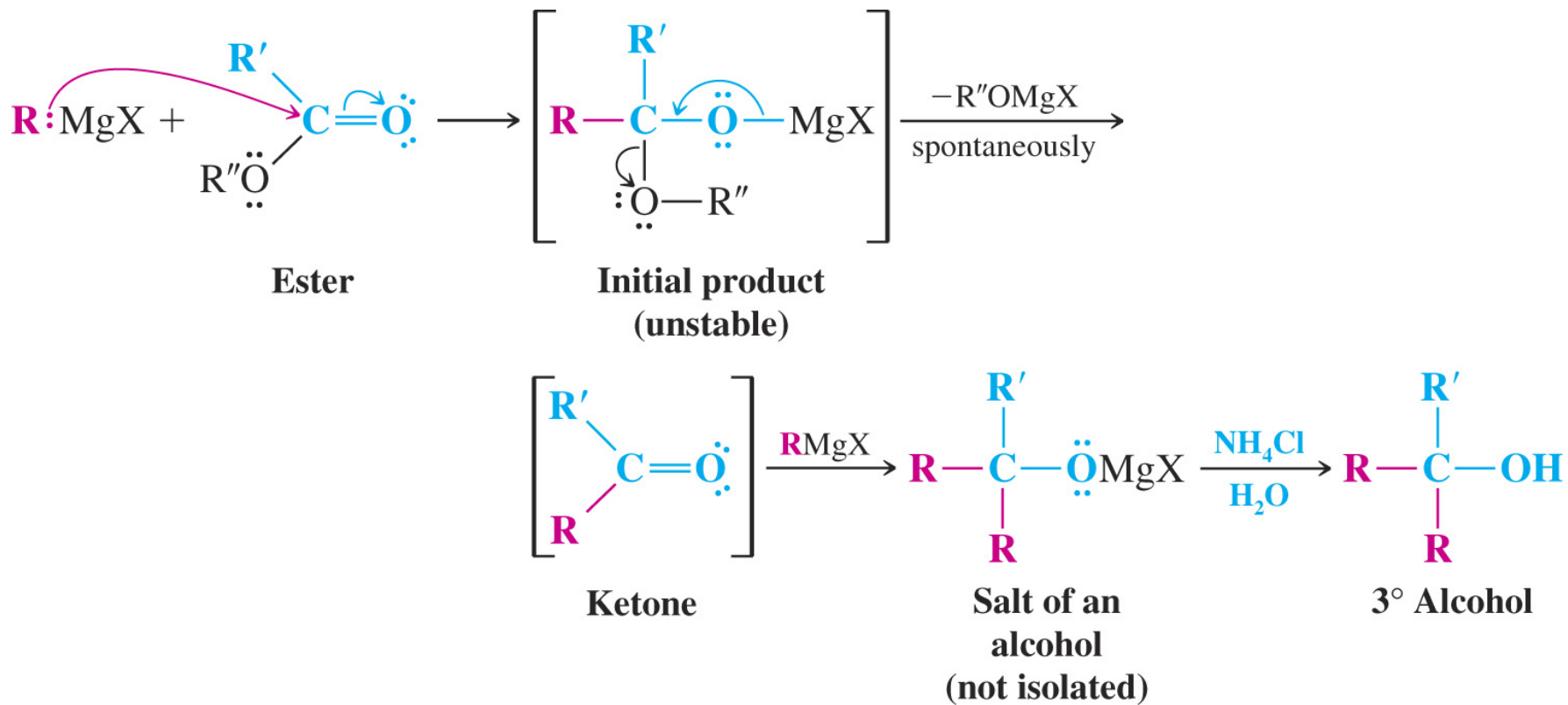
需從立體位阻小的位置攻入：



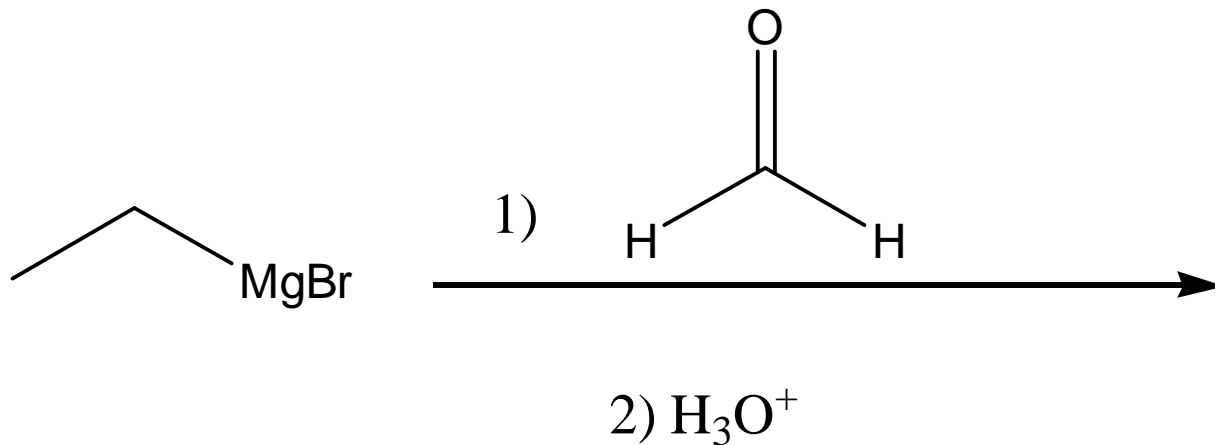
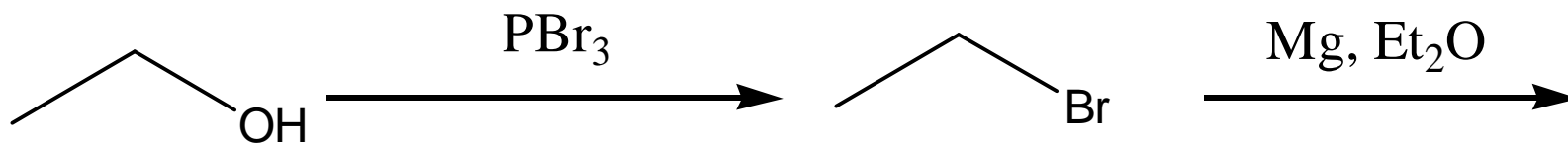
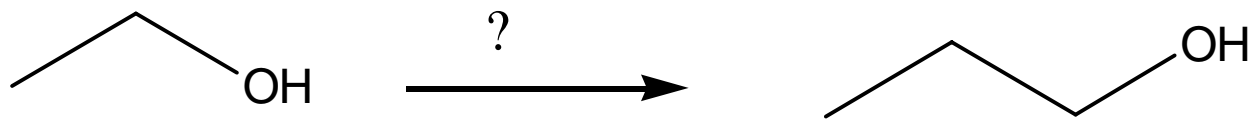
c) Grignard reagents與醛，酮酯的反應：

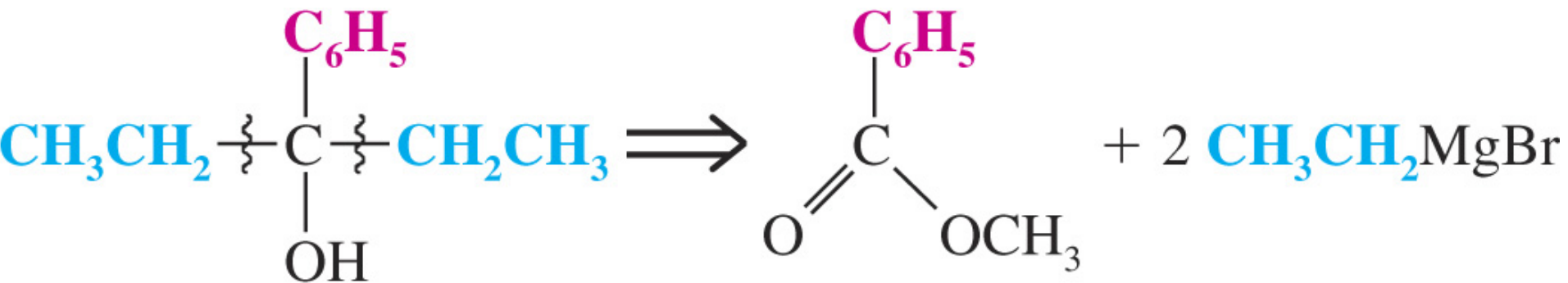
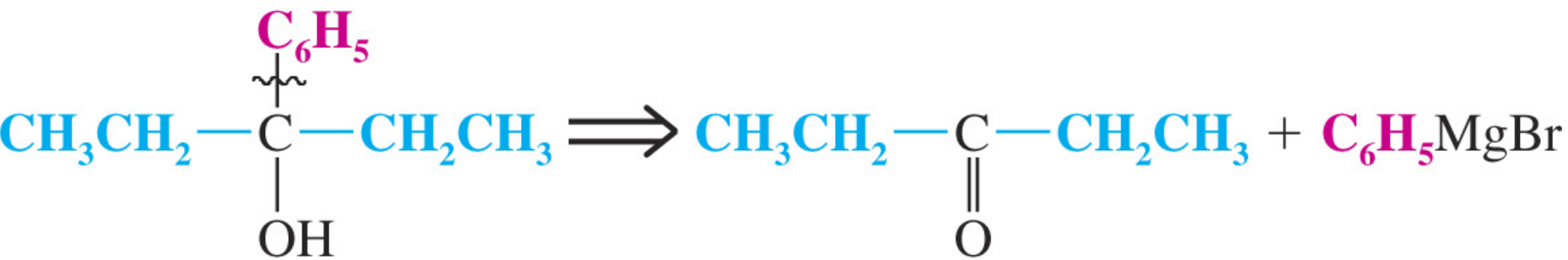


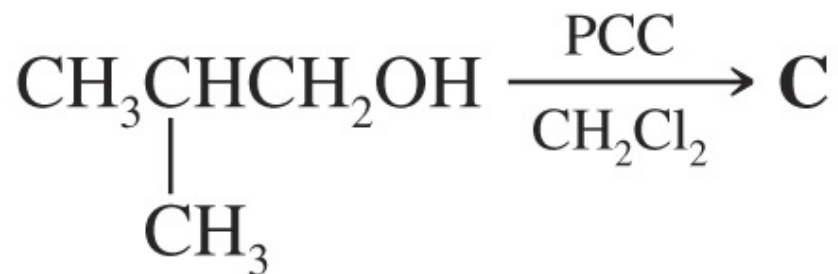
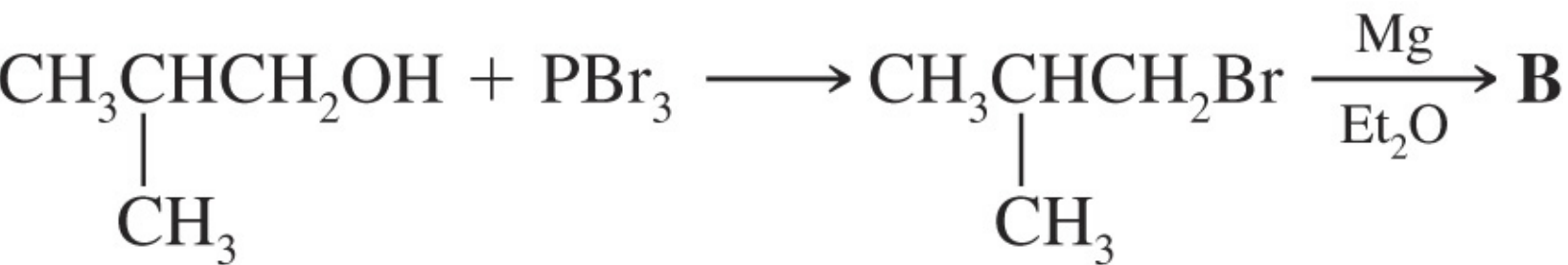


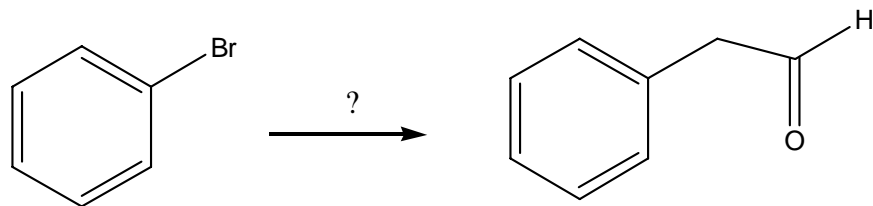


d) 利用 Grignard reagents 設計合成



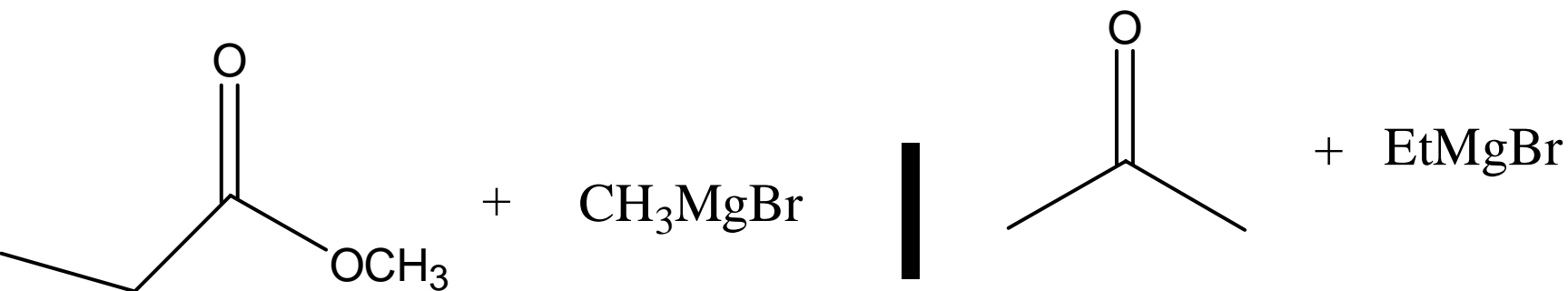
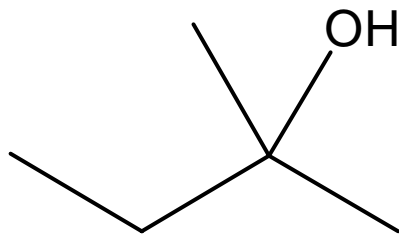


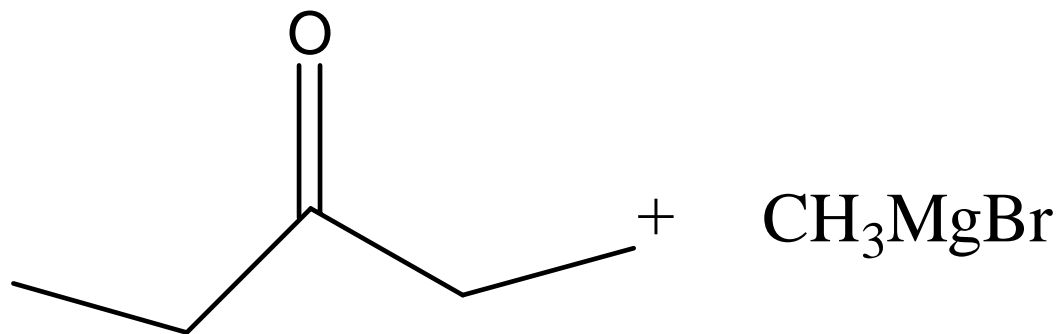
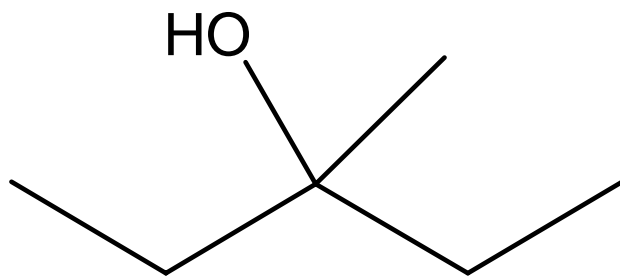


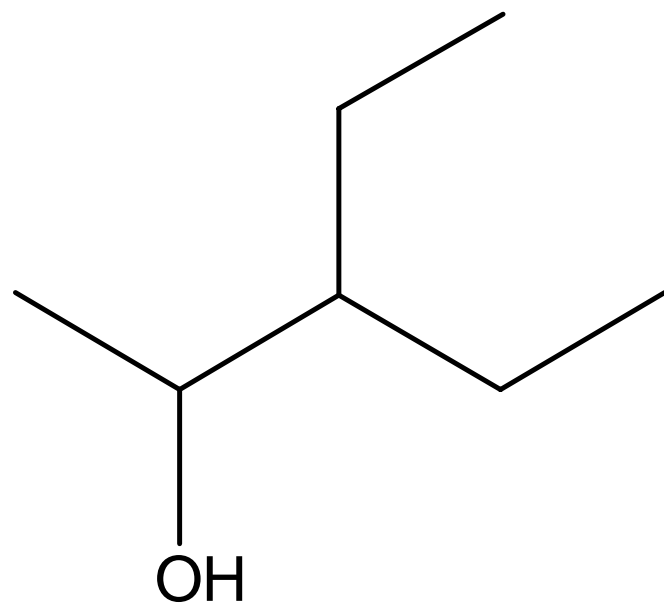


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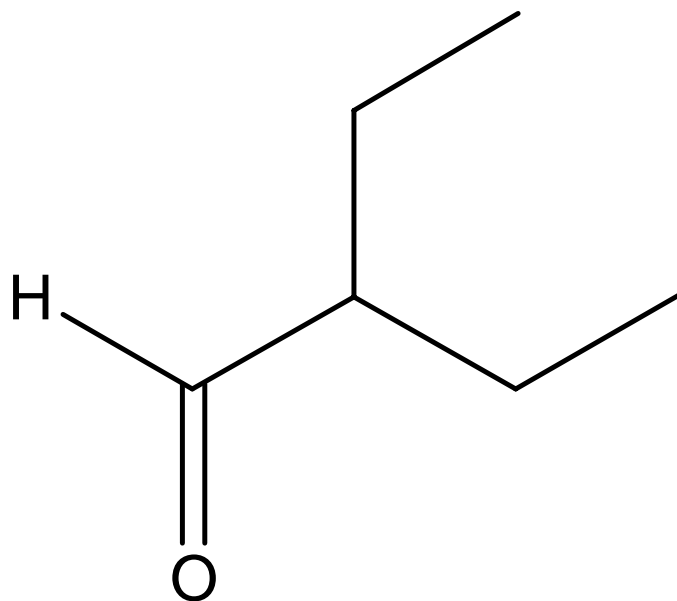
請選用合適的試劑製備下列化合物

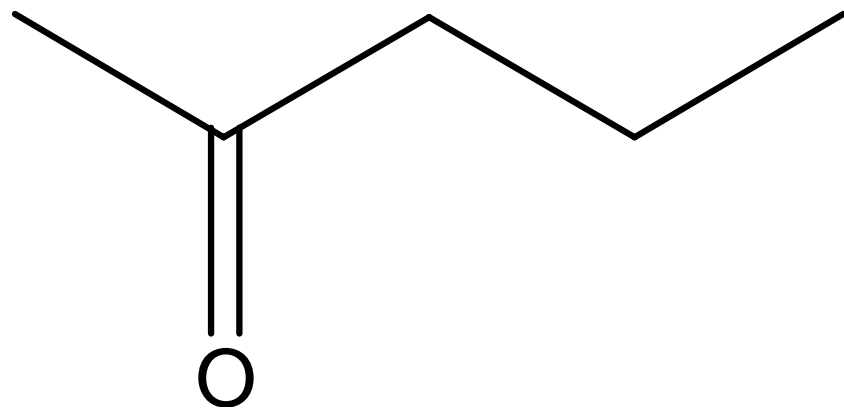
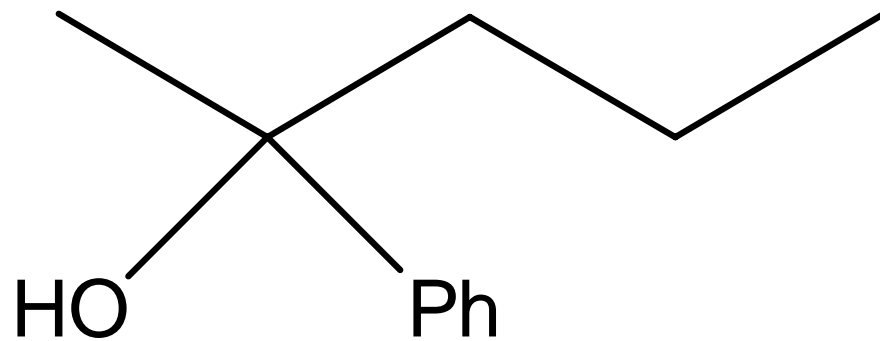


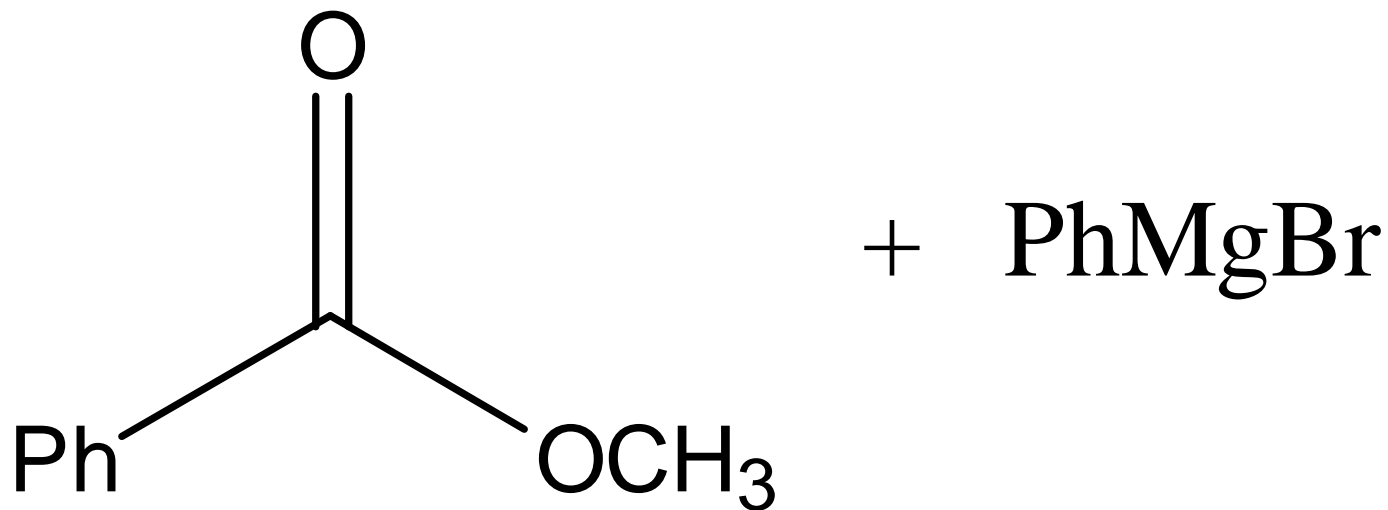
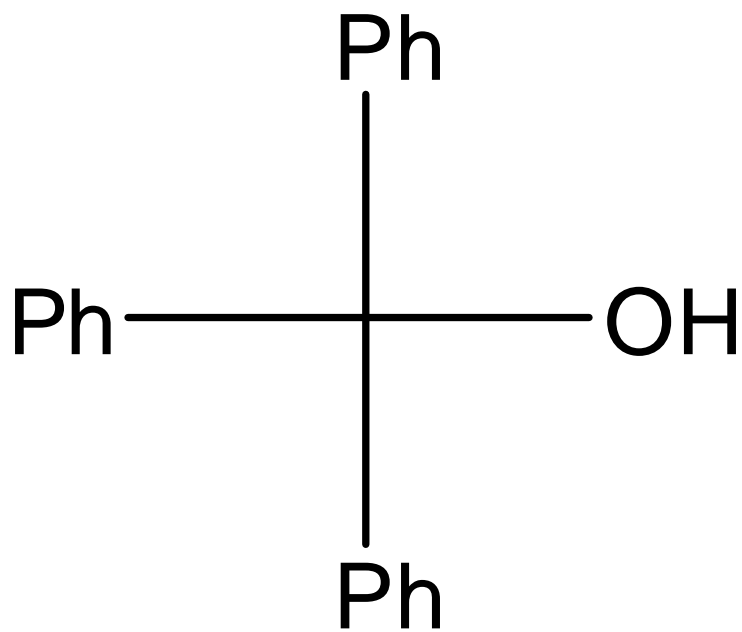




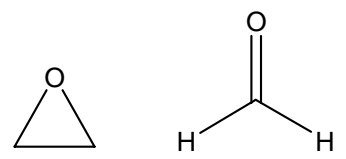
+



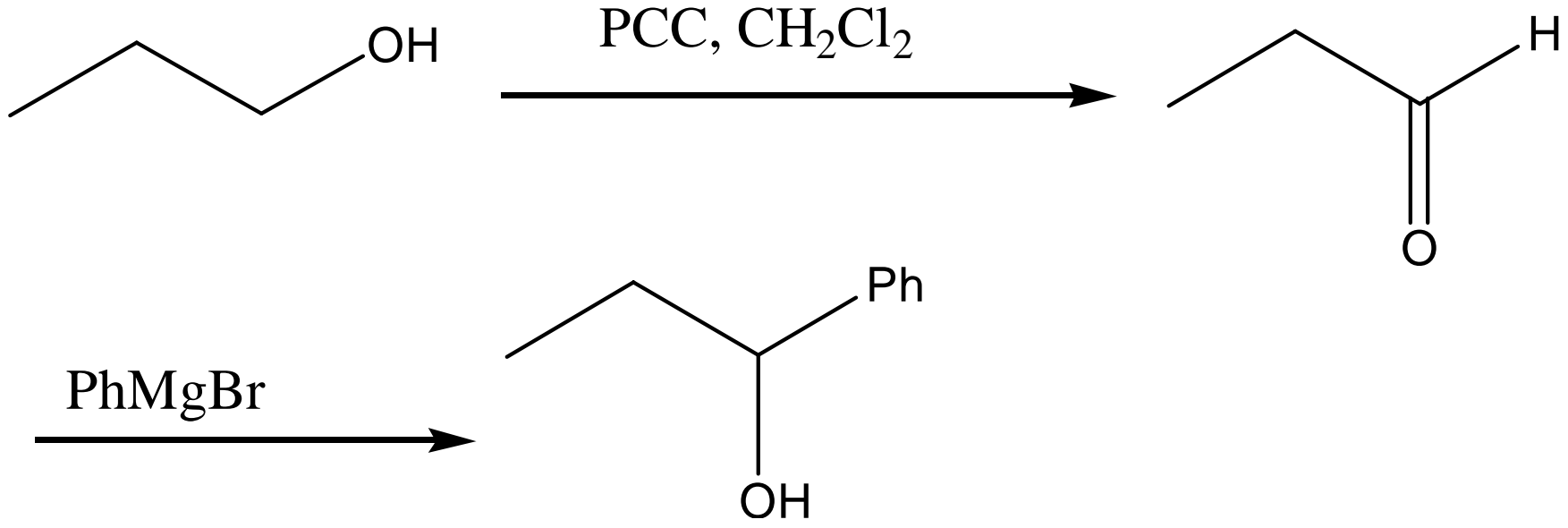


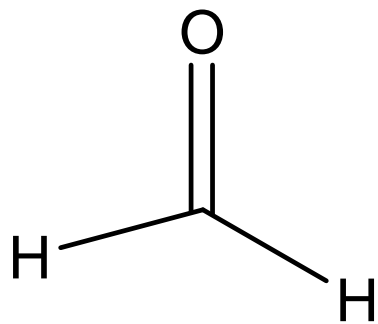


用不超過四個碳的醇或酯，PhMgBr，

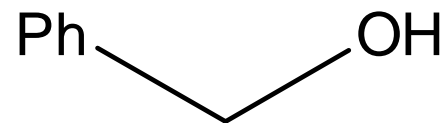


合成下列化合物。





PhMgBr



PCC

