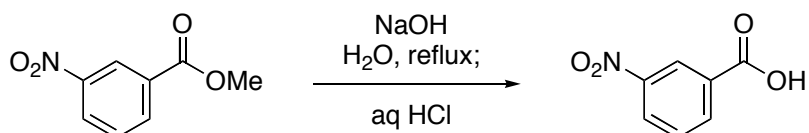


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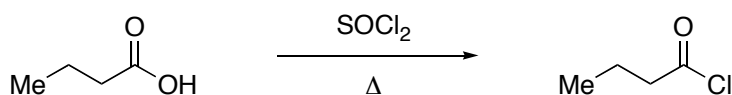
担当：吉村 文彦 (医薬品製造化学分野)

以下の反応の反応機構を電子の流れがわかるように、別紙に矢印を使って記せ。

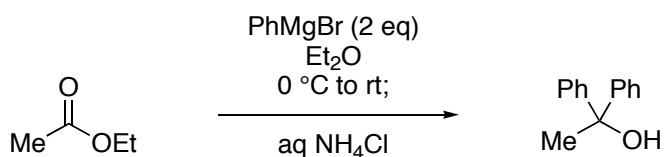
1.



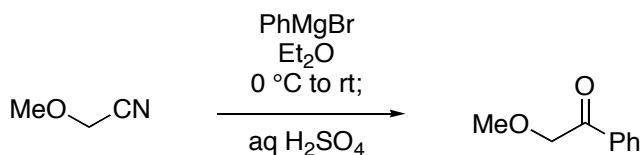
2.



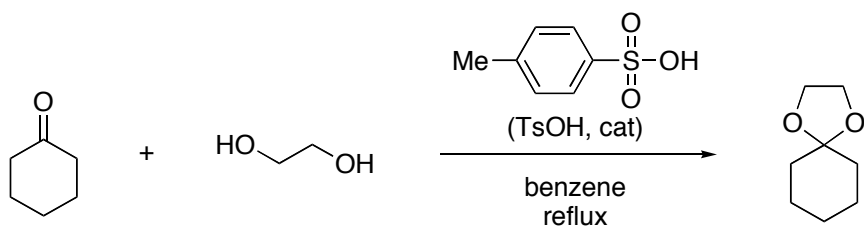
3.



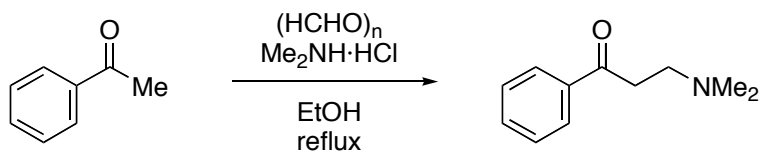
4.



5.



6.



1.

表① 一般的な元素の電気陰性度

H						
2.1						
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca					Br
0.8	1.0					2.8
						I
						2.5

ヒント : A: Addition of hydroxide ion to the carbonyl group to form a tetrahedral intermediate. B: Elimination of methoxide ion helped by the oxygen lone pair. C: Deprotonation. pK_a AcOH = 4.8, H₂O = 15.7. D: Protonation on workup. pK_a H₃O⁺ = -1.7.

2.

ヒント : A: Attack of a carboxylic acid to SOCl₂ forms a mixed anhydride. B: Addition of chloride ion to the carbonyl group to form a tetrahedral intermediate. C: Formation of an acylium ion. D: Addition of chloride ion to the acylium ion.

3.

ヒント : A: Addition of PhMgBr to the carbonyl group of the ester to form a tetrahedral intermediate. B: Elimination of ethoxide ion to form a ketone. C: Addition of PhMgBr to the more reactive ketone to form a tertiary alkoxide.

4.

ヒント : A: Addition of PhMgBr to the nitrile forms an imine anion. B: Addition of water to the iminium ion gives a hemiaminal. C: Protonation occurs on a more basic amino group. $\text{p}K_{\text{a}}$ $\text{H}_3\text{O}^+ = -1.7$, $\text{EtNH}_3^+ = 10.6$. D: Elimination of ammonia helped by the oxygen lone pair. E: Deprotonation.

5.

ヒント : A: Activation of the carbonyl group by protonation. B: Addition of ethylene glycol to the activated carbonyl group. C: Proton transfer. D: Elimination of water helped by the oxygen lone pair. E: Intramolecular addition of the second hydroxy group.

6.

ヒント : Mannich reaction. A: Protonation of formaldehyde followed by addition of Me_2NH to the carbonyl group. B: Proton transfer followed by elimination of water to form an iminium ion. C: Tautomerization of the ketone to form an enol. D: Attack of the electron-rich enol to the iminium ion.