

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, H_2O = 15.7. D: Protonation on workup. pK_a H_3O^+ = -1.7.

2.

ヒント : A: Attack of a carboxylic acid to $SOCl_2$ 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.

7.

ヒント : A: 1,2-Addition of MeMgBr to the carbonyl group. B: Protonation followed by elimination of water helped by the oxygen lone pair of the ethoxy group. C: Addition of water. D: Proton transfer followed by elimination of EtOH.

8.

ヒント : Aldol reaction. A: Deprotonation of the ketone to form an enolate. B: Attack of the enolate to an aldehyde. C: Protonation and deprotonation followed by elimination of a hydroxy ion.

9.

ヒント : Dieckmann condensation. A: Deprotonation of the ester to form an enolate. B: Intramolecular addition of the enolate to the other ester. C: Elimination of ethoxide ion. D: pK_a $RCOCH_2CO_2R = 10.7$, $EtOH = 16$.

10.

ヒント : A: Acid-catalyzed formation of an enol. B: Bromination of the electron-rich enol.

1 1.

ヒント: Wittig reaction. A: Addition of the ylide to the carbonyl group to form a betaine. B: Attack of the alkoxide to the phosphonium cation to form an oxaphosphetane. C: Irreversible elimination of $\text{Ph}_3\text{P}=\text{O}$.

1 2.

ヒント: Wolff-Kishner reduction. A: Addition of H_2NNH_2 to the carbonyl group. B: Proton transfer followed by elimination of hydroxide ion to form a hydrazone. C: Deprotonation of the hydrazone. D: Elimination of N_2 , an extremely good leaving group.

13.

ヒント: Gabriel synthesis. A: pK_a $RCONHCOR = 9.6$, $HCO_3^- = 10.3$. B: Alkylation. C: Addition of H_2NNH_2 to the imide to form a hydrazide. D: Intramolecular addition of the amino group of the hydrazide to the amide carbonyl to release benzylamine.

14.

ヒント: Baeyer-Villiger oxidation. A: Activation of the carbonyl group by protonation. B: Addition of $mCPBA$ to the carbonyl group. C: 1,2-Alkyl shift helped by the oxygen lone-pair with cleavage of the peroxide to form a lactone.

15.

ヒント : Hofmann rearrangement. A: pK_a $RCONH_2 = 17$, $H_2O = 15.7$. B: Chlorination of the amide anion. C: Deprotonation. D: The anion on the nitrogen atom induces migration of the aromatic ring with cleavage of the N-Cl bond to form an isocyanate. E: Addition of hydroxide ion to the isocyanate. F: Decarboxylation.

16.

ヒント : A: Allylation of the phenol. B: [3,3] Sigmatropic rearrangement (Claisen rearrangement). C: Aromatization.

17.

ヒント : A: Diels-Alder reaction. B: Retro Diels-Alder reaction.

18.

ヒント : A: Hydroboration through a four-membered transition state. B: Attack of a hydroperoxide anion to the borane to form an ate complex. C: Migration of an alkyl group. D: Hydrolysis of the borate.

19.

ヒント : A: Formation of nitrous anhydride. B: Addition of the aniline to nitrous anhydride. C: Proton transfer followed by elimination of water to form a diazonium salt. D: Addition of electron-rich dimethylaniline to the diazonium salt. E: Aromatization.

20.

ヒント : A: Deprotonation of the malonate to form an enolate (pK_a $RO_2CCH_2CO_2R = 13$, $H_2 = 35$). B: Nucleophilic addition of the enolate to the electron-deficient aromatic ring. C: Elimination of fluoride ion.

2 1.

ヒント: Pictet-Spengler reaction. A: Formation of an imine. B: Addition of an electron-rich aromatic ring to the iminium ion followed by aromatization.

2 2.

ヒント: Eschweiler-Clarke methylation (A-C) and Cope elimination (D-E). A: Addition of the amine to formaldehyde followed by dehydration to form an iminium ion. B: Hydride transfer from a formate anion to the iminium ion with generation of CO₂. C: Iteration of the same steps. D: Oxidation of the tertiary amine to form an *N*-oxide. E: *syn*-Elimination.

23.

ヒント : A: 1,3-Dipolar cycloaddition of ozone to the olefin. B: Heterolytic cleavage of the initial ozonide. C: Recombination of the resulting 1,3-dipole and the aldehyde to form an ozonide. D: Reductive cleavage of the O-O bond of the ozonide with Me_2S .

24.

ヒント : Jones oxidation. A: Hydration of CrO_3 . B: Attack of the alcohol to H_2CrO_4 . C: Elimination of H_2CrO_3 .