國立中正大學
113 學年度碩士班招生考試
試 題

［第 3 節］

科目名稱	有機無機化學
系所組別	化學暨生物化學系

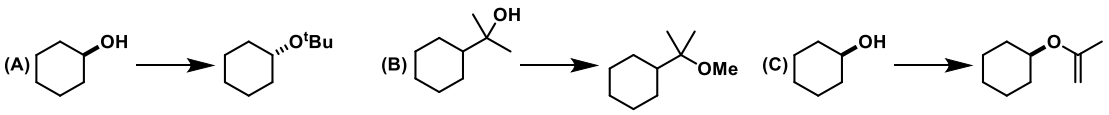
－作答注意事項－

※作答前請先核對「試題」、「試卷」與「准考證」之系所組別、科目名稱是否相符。

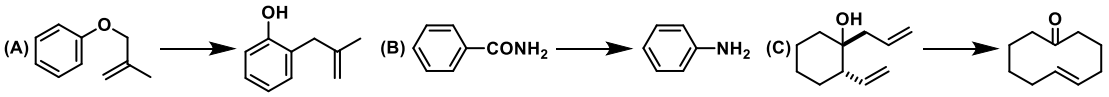
1. 預備鈴響時即可入場，但至考試開始鈴響前，不得翻閱試題，並不得書寫、畫記、作答。
2. 考試開始鈴響時，即可開始作答；考試結束鈴響畢，應即停止作答。
3. 入場後於考試開始 40 分鐘內不得離場。
4. 全部答題均須在試卷（答案卷）作答區內完成。
5. 試卷作答限用藍色或黑色筆（含鉛筆）書寫。
6. 試題須隨試卷繳還。

(有機化學部分共有 22 題綜合題型問題)

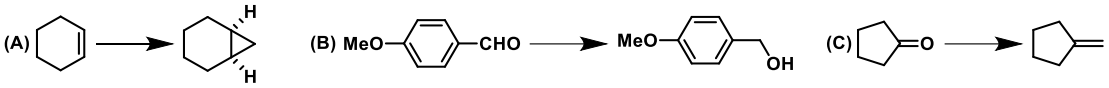
1. (1 point) Which of the following transformations can be carried out by the Williamson ether synthesis reaction?



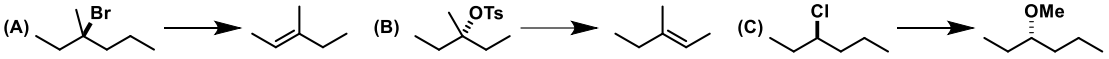
2. (1 point) Which of the following transformations can be carried out by the Claisen rearrangement?



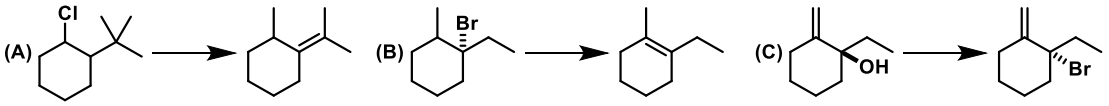
3. (1 point) Which of the following transformations can be carried out by the Simmons-Smith reaction?



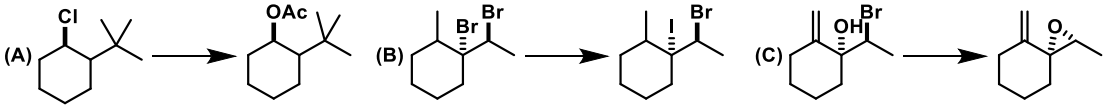
4. (1 point) Which of the following transformations is the best result of an E2 reaction?



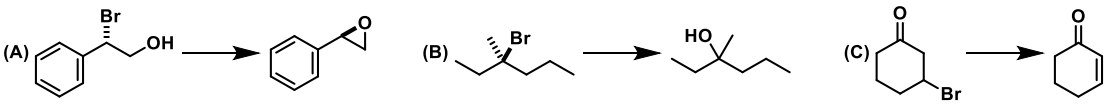
5. (1 point) Which of the following transformations is the result from an E1 reaction?



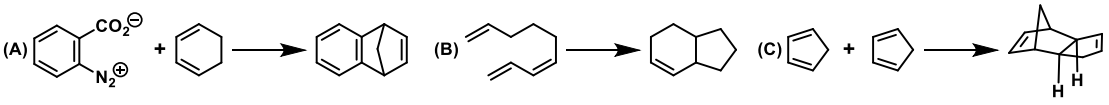
6. (1 point) Which of the following transformations is the result from a S_N2 reaction?



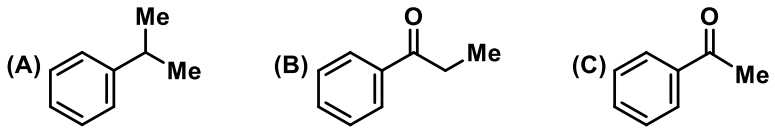
7. (1 point) Which of the following transformations is the result from a S_N1 reaction?



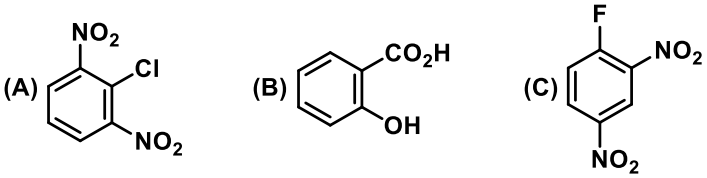
8. (1 point) Which of the following transformations can be carried out by the Diels-Alder reaction?



9. (1 point) Which of the following compound is cumene?

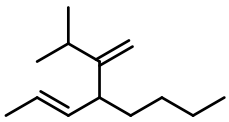


10. (1 point) Which of the following compound is called Sanger's reagent?

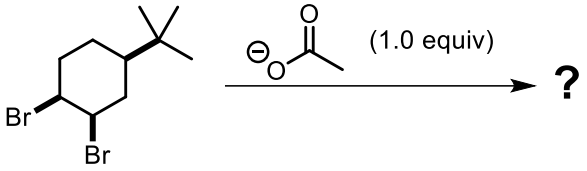


11. (3 points) Give structure each of the following names: (a) toluene, (b) ethyl acetate, and (c) tetrahydrofuran.

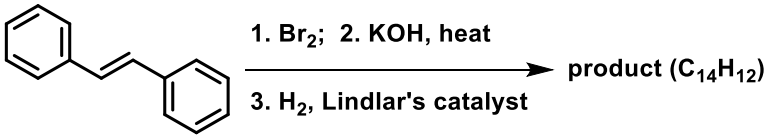
12. (3 points) What is the IUPAC name for the below compound?



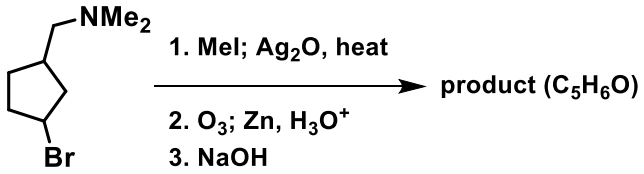
13. (3 points) Give the product of the below reaction transformation:



14. (3 points) Give the final product of the below 3-step synthesis:



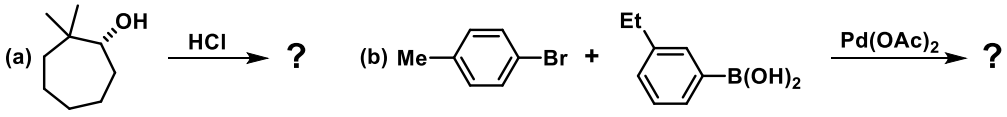
15. (3 points) Give the final product of the below synthesis:



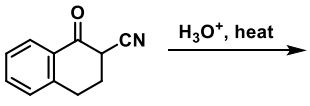
16. (3 points) Predict the product for each reaction below:

17. (3 points) Propose a structure for an unknown organic compound that fits the following proton NMR spectral data: $C_6H_5NCl_2$; δ 7.14 (d, 2H), 6.57 (t, 1H), 4.40 (broad s, 2H)

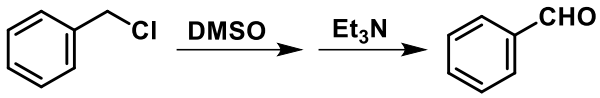
18. (3 points) Give structures of the product for each below reaction:



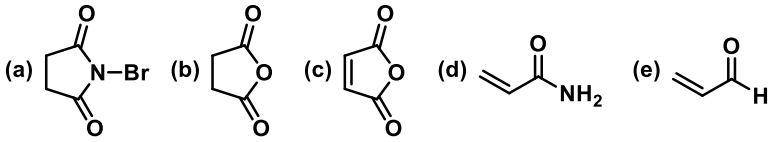
19. (3 points) Give the product of the following reaction:



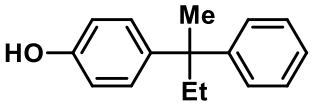
20. (3 points) The below reaction is called Kornblum oxidation. Provide your mechanism for such functional group transformation.



21. (5 points) What are common names of the following compounds:



22. (5 points) How would you synthesize the following substance, starting from benzene as the source of the aromatic ring?

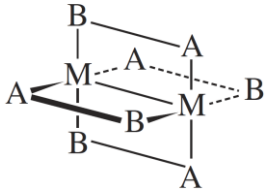


(無機化學部分共有 25 題綜合題型問題)

I. Multiple-Choice Questions (單選題，每題 2 分)

23. What is the point group for the following structure?

(A) D_{2h}
(B) C_{2v}
(C) D_{2d}
(D) C_{4v}
(E) D_{4h}



24. Br_2^+ is red and I_2^+ is bright blue. What electronic transition is most likely responsible for absorption in these ions?

(A) $\sigma^* \rightarrow \pi^*$
(B) $\sigma \rightarrow \pi$
(C) $\sigma \rightarrow \pi^*$
(D) $\pi \rightarrow \sigma^*$
(E) $\pi^* \rightarrow \sigma^*$

25. Which of the following equations about symmetry elements is ***not*** true?
(A) $C_n^2 = S_n^2$
(B) $S_1 = \sigma$
(C) $S_2 = i$
(D) $C_2^2 = S_4^2$
(E) $C_2 \times \sigma_v\,(xz) = \sigma_v'\,(yz)$

26. Select the shortest C—O bond distance: $[Ti(CO)_6]^{2-}$, $[V(CO)_6]^{-}$, $Cr(CO)_6$, $[Mn(CO)_6]^{+}$, $[Fe(CO)_6]^{2+}$
(A) $Cr(CO)_6$
(B) $[Mn(CO)_6]^{+}$
(C) $[V(CO)_6]^{-}$
(D) $[Fe(CO)_6]^{2+}$
(E) $[Ti(CO)_6]^{2-}$

27. How many isomers (without considering ring conformations) are there for octahedral $[Co(dien)_2]^{3+}$
(*hint*: dien = diethylenetriamine, a tridentate ligand)
(A) 3 : *mer*-Λ , *mer*-Δ , *fac*
(B) 3 : *mer*, *fac*-Λ , *fac*-Δ
(C) 4 : *mer*-Λ , *mer*-Δ , *fac*-Λ , *fac*-Δ
(D) 4 : *mer*-α , *mer*-β , *fac*-Λ , *fac*-Δ
(E) 4 : *mer*-α , *mer*-β , *fac*-α , *fac*-β

28. Which of the following complexes has the least unpaired electrons but largest ligand filed stabilization energy?
$[Cu(H_2O)_6]^{2+}$, $[Cr(CN)_6]^{4-}$, $[Fe(H_2O)_6]^{3+}$, $[Co(NO_2)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$
(A) $[Cu(H_2O)_6]^{2+}$
(B) $[Cr(CN)_6]^{4-}$
(C) $[Fe(H_2O)_6]^{3+}$
(D) $[Co(NO_2)_6]^{4-}$
(E) $[Co(NH_3)_6]^{3+}$

29. For the free-ion term ^3D (d^3), what are the correct values of L, M_L, S, M_S, and the lowest energy of J ?
(A) $L = 3$; $S = 3/2$; $M_L = -3, -2, -1, 0, 1, 2, 3$; $M_S = -3/2, -1/2, 1/2, 3/2$; $J = 3$
(B) $L = 4$; $S = 1$; $M_L = -2, -1, 0, 1, 2$; $M_S = -1, 0, 1$; $J = 5/2$
(C) $L = 2$; $S = 1/2$; $M_L = -2, -1, 0, 1, 2$; $M_S = -1/2, 1/2$; $J = 3/2$
(D) $L = 2$; $S = 3/2$; $M_L = -2, -1, 0, 1, 2$; $M_S = -3/2, -1/2, 1/2, 3/2$; $J = 5/2$
(E) $L = 3$; $S = 1/2$; $M_L = -3, -2, -1, 0, 1, 2, 3$; $M_S = -1/2, 1/2$; $J = 3/2$

30. Given a dimeric complex with the chemical formula, $(\eta^5\text{-}C_5H_5)(CO)_2\mathbf{M{=}M}(CO)_2(\eta^5\text{-}C_5H_5)$, identify the 2nd row transition metal based on the 18 electron rule.

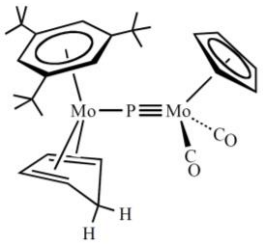
(A) M = Ta
(B) M = Ru
(C) M = Tc
(D) M = Re
(E) M = Mo

31. Which of the following electron configurations is ***not*** correct?

(A) Ta^{3+} : $[Xe]4f^{14}5d^2$
(B) Cr^{3+} : $[Ar]3d^3$
(C) Ru^{2+}: $[Kr]4d^6$
(D) Ce^{4+}: $[Xe]4f^1$
(E) Sb^{3+} : $[Kr]5s^24d^{10}$

32. The NMR signals of the molybdenum complex as shown below are given at δ: 5.46; 5.28; 5.15; 4.22; 2.56~2.78; and 1.31 ppm. What would be the most likely integration ratio accordingly?

(A) 2 : 5 : 3 : 2 : 2 : 27
(B) 3 : 5 : 2 : 2 : 27 : 2
(C) 5 : 2 : 2 : 27 : 2 : 3
(D) 5 : 2 : 27 : 2 : 2 : 3
(E) 3 : 2 : 2 : 2 : 5 : 27



II. Multiple Selection Questions (複選題，每題 2 分，全對才計分)

33. Which of the following symmetry elements should not be included in chiral compounds?

(A) an improper rotation axis (S_n)
(B) a rotation axis (C_n)
(C) an inversion center (i)
(D) a plane of symmetry (σ)
(E) the identity (E)

34. Which of the followings are correct?

(A) X－O length: $ClO_3^- > BrO_3^- > IO_3^-$
(B) O－X－O angle: $ClO_3^- > BrO_3^- > IO_3^-$
(C) Bond angle: HOH > HOF > FOF
(D) X－Sb－X angle: $SbCl_3 > SbBr_3 > SbI_3$
(E) P－F_{axial} length: $PF_2(CH_3)_3 > PF_3(CH_3)_2 > PF_4(CH_3)$

35. Which d^n configurations ***would not*** show Jahn-Teller splitting for the tetrahedral metal complexes (ignore possible low-spin cases)
    (A) d^2
    (B) d^3
    (C) d^4
    (D) d^5
    (E) d^7

36. Which of the following statements regarding the elementary reactions of organometallic complexes are correct?
    (A) For a reductive elimination reaction, the metal center undergoes a $2e^-$ reduction to form a new σ-bond between two ligands on the metal.
    (B) Reductive elimination is basically the same as β-elimination reaction.
    (C) For an oxidative addition process, the oxidation state of the metal center decreases by 2 unit to give two new metal–ligand bonds.
    (D) The reverse reaction of migratory insertion is β-elimination.
    (E) Olefin metathesis is a commonly occurring metathesis reaction that takes place between two alkenes.

37. Which of the followings are correct?
    (A) The number of radial nodes for a 3*d* orbital is 2.
    (B) The number of angular nodes for a 4*f* orbital is 3.
    (C) There 4 lines in the Balmer series of hydrogen atom spectrum.
    (D) There are at most 10 electrons in an atom having quantum numbers of ***n*** = 5 and ***l*** = 3.
    (E) The main cause of ***lanthanide contraction*** is the steady decrease in ionization energy of lanthanoids as their atomic number increases.

III. Fill in the blanks for the following questions. (填空題，每空格 2 分)

38. _____ describes the influence of inner electrons on the effective nuclear charge felt by outer electrons.

39. Suggest the geometry of a square planar complex after a 2-electron oxidative addition reaction?
    _____

40. Reductive elimination is accompanied by _____ (*increase* or *decrease*) in the oxidation state of the metal.

41. For the complex $[Ru(NH_3)_6]^{3+}$, assign the spin multiplicity of the metal center. _____

42. Following the previous question, what is the magnetism of the complex? _____

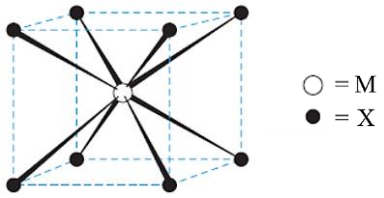
43. How many isomeric structures are possible for IF_3O_2? _____

44. Following the previous question, what is the point group designations of the structure with the lowest energy. _____

45. How many total vibrational modes does a planar $PtCl_4^{2-}$ ion have? _____

46. How many C—O stretching bands would you predict for the trigonal bipyramidal *trans*-$Ru(CO)_2(PEt_3)_3$? _____

47. Using the diagram of unit cell shown below, determine the formula of the compound. _____ (open circle = cationic M, closed circles = anionic X)



IV. Some Character Tables

C_{nv} Groups

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		$x^2 - y^2$
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y), (R_x, R_y)$	(xz, yz)

D_{nh} Groups

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		$x^2 - y^2$
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

D_{nd} Groups

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$		
A_{1g}	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	−1	1	1	−1	R_z	
E_g	2	−1	0	2	−1	0	(R_x, R_y)	$(x^2 - y^2, xy)$ (xz, yz)
A_{1u}	1	1	1	−1	−1	−1		
A_{2u}	1	1	−1	−1	−1	1	z	
E_u	2	−1	0	−2	1	0	(x, y)	

D_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4\sigma_d$		
A_1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	1	1	1	−1	−1	R_z	
B_1	1	−1	1	−1	1	1	−1		
B_2	1	−1	1	−1	1	−1	1	z	
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	−2	0	0	(x, y)	
E_2	2	0	−2	0	2	0	0		$(x^2 - y^2, xy)$
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	−2	0	0	(R_x, R_y)	(xz, yz)