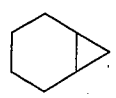
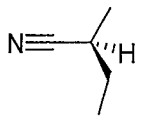
國立中山大學104學年度碩士暨碩士專班招生考試試題

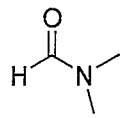
科目名稱：有機化學及無機化學【化學系碩士班】　　題號：422001

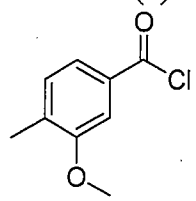
※本科目依簡章規定「不可以」使用計算機(問答申論題)　　

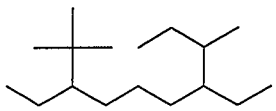
1. (10%) Chlorine trifluoride could be produced from fluorination of chlorine. (1) Give a balanced chemical equation for this reaction. (2) What is the molecular geometry of chlorine trifluoride? (3) Is this molecule polar or non-polar? (4) Are the bond distances between chlorine and fluorine atoms all identical, and why or why not? (5) Are the bond angles of chlorine trifluoride larger or smaller than or equal to those of iodine trifluoride, and why?
2. (14%) (1) Give the Lewis structure of CO. (2) In $Cr(CO)_6$, explain why CO binds to Cr at C instead of O. (3) How many CO stretching bands can be observed in the IR spectrum of $Cr(CO)_6$? (4) Assign Mulliken symbol(s) to the IR band(s). (5) Compounds $[\mathbf{X}(CO)_6]^{2-}$ and $[\mathbf{Z}(CO)_6]^{+}$ are isoelectronic to $Cr(CO)_6$; what are **X** and **Z**? (6) Arrange the increasing order of C-O bond distances in $Cr(CO)_6$, $[\mathbf{X}(CO)_6]^{2-}$ and $[\mathbf{Z}(CO)_6]^{+}$.
3. (16%) Water coordinates to transition metals to give aqua complexes. (1) Give the Lewis structure of water. (2) Is water a pure sigma-donor, pi-base or pi-acid ligand? (3) The crystal field stabilization energy of $[Co(H_2O)_6]^{2+} = x\text{Dq}$, x = ? (4) Give the *d*-orbital diagram of $[Co(H_2O)_6]^{2+}$ with complete electron filling and orbital labeling. (5) Estimate the spin-only magnetic moment of $[Co(H_2O)_6]^{2+}$ in Bohr Magneton. (6) What is the point group in determining the electronic structure of $[Co(H_2O)_6]^{2+}$. (7) How many *d-d* transitions can be found for $[Co(H_2O)_6]^{2+}$?
4. (10%) Complex $Ta(CH_2Ph)_5$ is a stable, deep red crystalline solid while $Ta(CH_2CMe_3)_5$ is a short-lived species that decomposes to give an orange, sublimable, crystalline product. (1) Explain why the stability difference in these complexes occurs. (2) Interpret how $Ta(CH_2CMe_3)_5$ decomposes. (3) Give the structure of the orange crystalline complex. (4) Calculate the electron count of this orange complex. (5) What is (are) the significant feature(s) of this orange complex?
5. (12%) Give the IUPAC names of the following compounds.

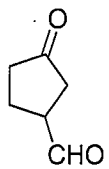
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

6. (12%) Please write the structures of products (A), (B) and (C) with specific stereochemistry and explain the stereochemistry of these reactions with reasonable mechanisms.

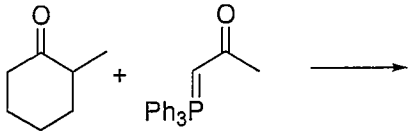
(2*S*,3*R*)-3-bromobutan-2-ol $\xrightarrow{HBr}$ 2,3-dibromobutane (meso)

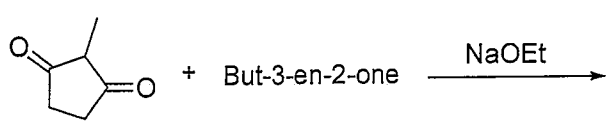
(A)

(2*R*,3*R*)-3-bromobutan-2-ol $\xrightarrow{HBr}$ 2,3-dibromobutane (racemate)

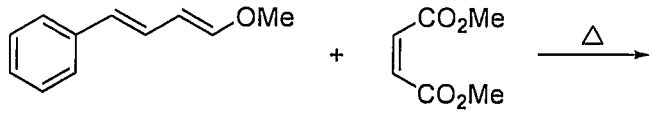
(B) and (C)

7. (15%) Predict the main products of the following reactions.

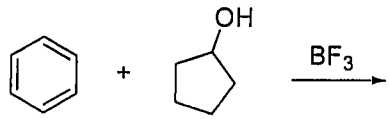
(a) 

(b) 

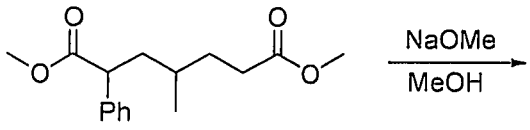
(c)



(d)



(e)



8. (11%) In an addition reaction, HBr adds to 1,3-butadiene to form a mixture of 3-bromobut-1-ene (1,2-addition) and 1-bromobut-2-ene (1,4-addition). At -80 °C, 3-bromobut-1-ene is the major product, and at 40 °C 1-bromobut-2-ene is the major product. Please answer the following questions according to the above description.

(a) Please indicate which the thermodynamic product is and which the kinetic product is. And explain why.

(b) According to the allyl cation intermediate, please explain the thermodynamic and kinetic control of the reaction.

(c) The reaction is known as an exothermic reaction. Please draw a energy-coordinate diagram to represent this reaction.