國立中央大學94學年度碩士班考試入學試題卷 共2頁第/頁所別:化學學系碩士班科目:有機化學與無機化學

- 1. 2-Bromopropane can undergo S_N2 , S_N1 , E2, or E1 reaction as the major reaction pathway, depending on the reaction conditions. Give one example for each of these four types of reactions for 2-bromopropane with reaction conditions (reagents, solvents, and temperature) and the structure of products. (10 pts)
- 2. When acetone is treated with anhydrous ammonia in the presence of anhydrous calcium chloride (a common drying agent), crystalline product **A** is obtained on concentration of the organic liquid phase of the reaction mixture.

These are spectral data for product A:

MS (m/z): 155 (M⁺), 140

IR (cm⁻¹): 3350 (sharp), 2850-2960, 1705

¹H NMR (δ): 2.3 (s, 4H), 1.7 (1H; disappears in D₂O), and 1.2 (s, 12H)

(a) What is the structure of A (assign the peaks for IR and NMR)? (5 pts)

(b) Propose a mechanism for formation of A (use curved arrows). (5 pts)

3. How would you convert compound **B** to compound **C**? (10 pts)

- 4. Explain the following observations.
 - (a) Cycloheptatrienone (**D**) is very stable. Cyclopentadienone (**E**) by contrast is quite unstable. (5 pts)

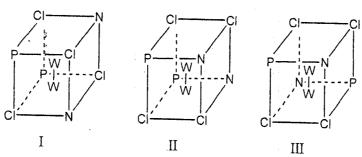
(b) The C-H bond dissociation energy in ethane, ethene, and ethyne is ethane < ethene < ethyne. (5 pts)

- (c) Compound F racemizes in base. (5 pts)
- (d) The order of basicity of these amines in aqueous solution is $Me_2NH > MeNH_2 > Me_3N$. (5 pts)

注:背面有試題

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- 5. Predict the structures of the following. (6 pts) (a) IOF₄ (b) XeOF₄ (c) XeF₈²⁻
- 6. Which compound has the smallest bond angle in each series? (4 pts) (a) OSF₂, OSCl₂, OSBr₂ (X-S-X angle); (b) PI₃, AsI₃, SbI₃
- Classify the following configuration as A, E or T in complexes having O_h symmetry. Some of these configurations represent excited states. (6 pts)
 (a) t_{2g}⁵ (b) t_{2g}³ e_g³
- 8. Identify the most likely second-row transition metal for each of the following:
 (a) M(PF₃)₂(NO)₂⁺ (linear M-N-O bond) (3 pts)
 (b) [M(CO)₄(µ₂-H)]₃ (3 pts)
- 9. Predict the relative order of IR_(NO) frequencies for the following compounds. (6 pts) $[Cr(CN)_5(NO)]^{4-}, [Mn(CN)_5(NO)]^{3-}, [Fe(CN)_5(NO)]^{2-}$
- 10. BrCH₂CH₂CH₂Mn(CO)₅ is formed by reaction of Mn(CO)₅ with 1,3-dibromopropane. However, the reaction does not stop here; the product reacts with additional Mn(CO)₅ to yield a carbene complex. Propose a structure for this complex and suggest a mechanism for its formation. (10 pts)
- 11. Three isomers of $W_2Cl_4(NHR)_2(PMe_3)_2$ are possible. Determine the point group of each. (6 pts)



12. BrF₃, I₂Cl₆ and even H₂SO₄ are widely used as nonaqueous solvents. They undergo significant autodissociation. Show the corresponding reaction. (6 pts)