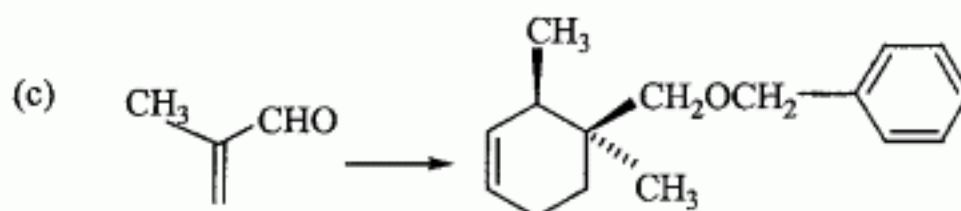
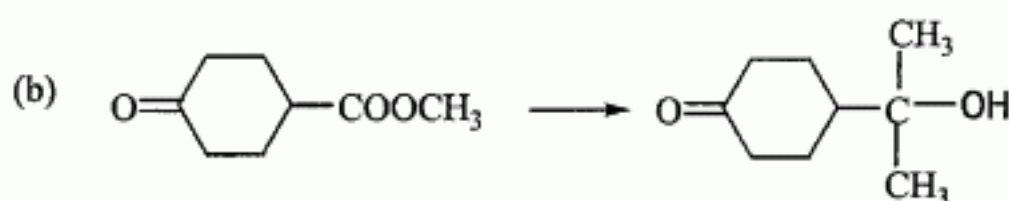
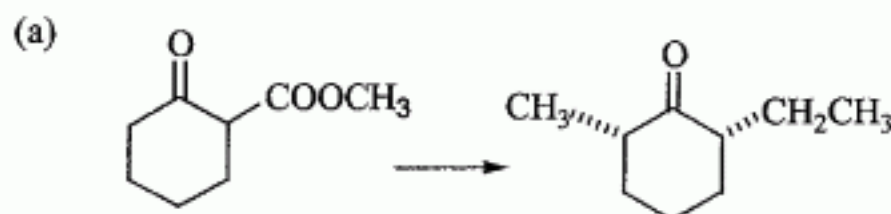


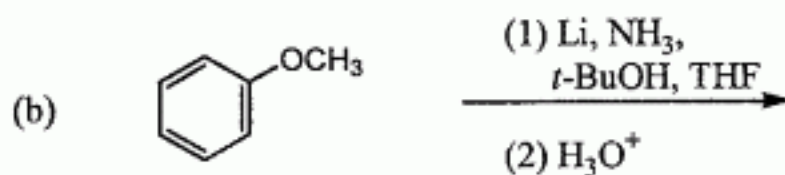
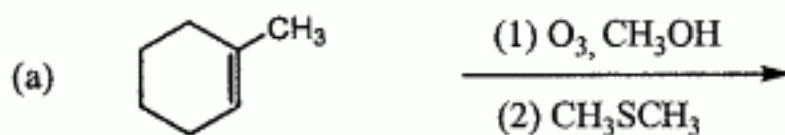
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科目_無機化學及有機化學_科號_0602, 0702_共_5_頁第_1_頁 *請在試卷【答案卷】內作答

1. In each case, provide a suitable synthesis. Show all intermediate products and all reagents. (15%)

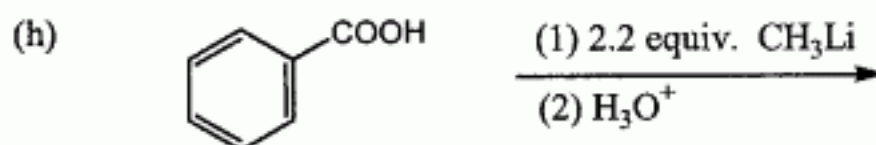
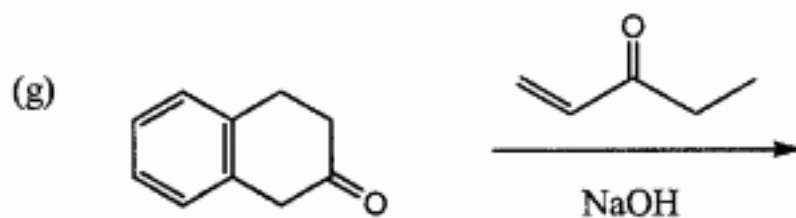
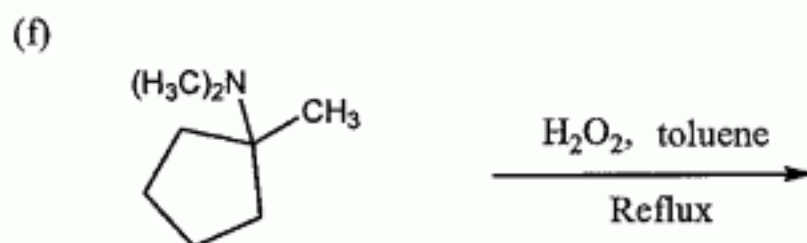
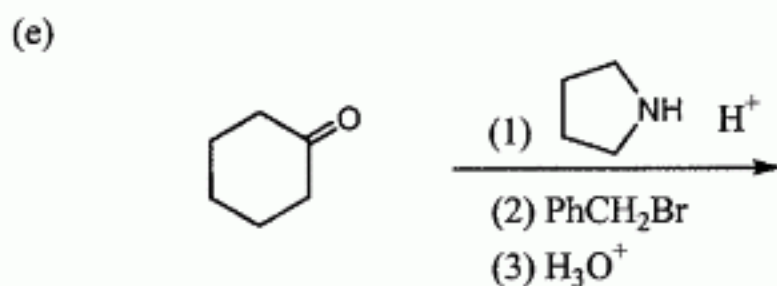
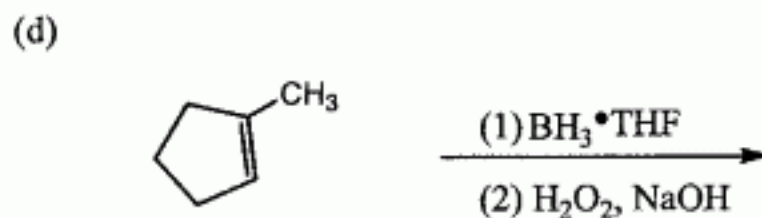
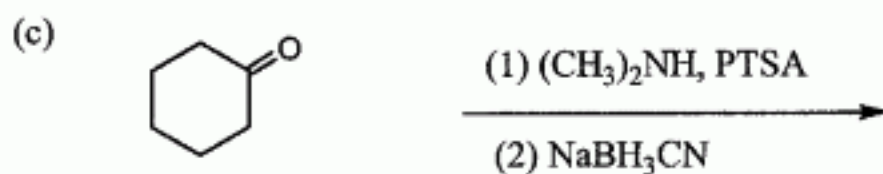


2. Give a structure consistent with each of the following sets of NMR data: (10%)
- (a) $C_5H_{10}Br_2$: δ 1.0 (singlet, 9H), 5.3 (singlet, 1H)
- (b) $C_9H_{11}Br$: δ 2.2 (quintet, 2H), 2.8 (triplet, 2H), 3.4 (triplet, 2H), 7.2 (singlet, 5H)
3. Predict the major product of the following reactions and also write stepwise reaction mechanism using the arrow formalism. (25%)

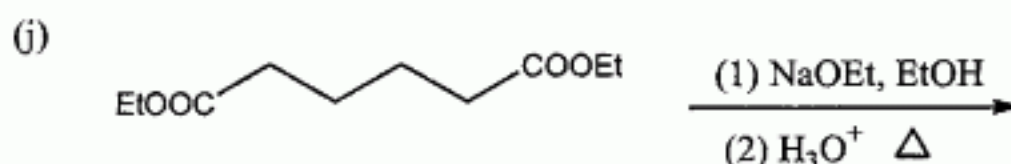


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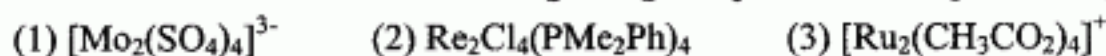
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4. Indicate the probable occupancy of σ , π and δ bonding and antibonding orbitals and the bond order for the following tetragonal prismatic complexes: (5%)



5. The *trans* effect in ligand substitution reactions on square planar complexes plays an important role in preparations of different isomers.

(1) What is the origin of *trans* effect? (5%)

(2) Please predict the products of the following reactions:

- $[\text{Pt}(\text{PPh}_3)_4]^{2+} + 2 \text{Br}^-$
- $[\text{PtCl}_4]^{2-} + 2 \text{PMe}_3$
- $\text{cis}-[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2]^{2+} + 2 \text{Cl}^-$

6. For a C_{4v} symmetry complex $[\text{CoCl}(\text{H}_2\text{O})_5]^+$, where the Cl^- ligand is on the z axis: (5%)

- Which orbitals will be displaced from their position in the octahedral molecular orbital diagram by π interactions with the lone pairs of the Cl^- ligand?
- Which orbital will move because the Cl^- ligand is not as strong as σ -donor as H_2O ?
- Sketch the qualitative molecular orbital diagram for this C_{4v} complex.

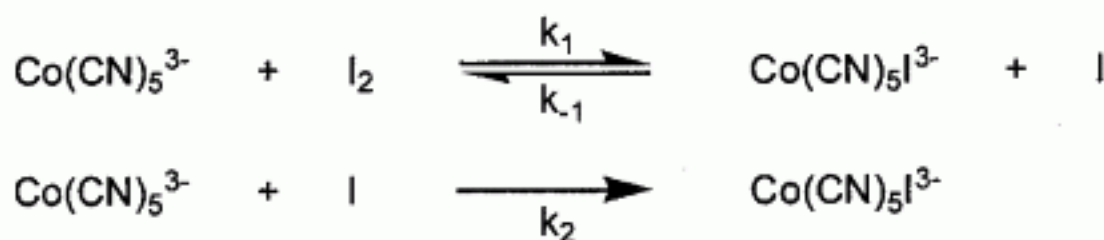
7. (1) Draw plausible structures and give the electron count of (a) $\text{Ni}(\eta^3\text{-C}_3\text{H}_5)_2$, (b) $\eta^4\text{-cyclooctadiene-}\eta^5\text{-cyclopentadienylcobalt}$, (c) $(\eta^3\text{-C}_3\text{H}_5)\text{Co}(\text{CO})_2$.
 (2) Using the 18-electron rule as a guide, indicate the probable number of carbonyl ligands in (a) $\text{W}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_n$, (b) $\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_n$, and (c)

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(5%)

8. Pentacyanocobalt(II) ($\text{Co}(\text{CN})_5^{3-}$) and iodine (I_2) react to give iodopentacyanocobalt(III) ($\text{Co}(\text{CN})_5\text{I}^{3-}$) as a product. The proposed mechanism has atomic iodine as a highly reactive intermediate (5%)



- (1) Write the chemical equation for the overall reaction.
 - (2) Derive the rate expression for the rate of formation of $\text{Co}(\text{CN})_5\text{I}^{3-}$ and for the rate of the loss of I_2
 - (3) Under what conditions will the rate of reaction become second-order overall?
 - (4) Under what conditions will the reaction product inhibit the rate?
9. Answer the following questions: (5%)
- (a) Write the formula for silicon dioxide, gallium oxide and tin sulfide.
 - (b) Why are the tin(IV) halide more volatile than the tin(II) halides?
 - (c) What is the mole ratio of lead(II) to lead(IV) in red lead (Pb_3O_4)?
10. About energy band in solids: (5%)
- (a) Draw energy band pictures for metal, semiconductor and insulator.
 - (b) Sodium has half-filled 3s orbitals while magnesium has fully filled 3s orbitals. Are they electrical conductors? Why?
 - (c) Whether the following solids are likely to be metal, semiconductor, or insulator: NaCl, sugar, and Ga. P-doped Si
11. Beryllium metal is amphoteric and reacts with aqueous NaOH to produce hydrogen gas and $\text{Be}(\text{OH})_4^{2-}$. (5%)
- (a) Write a balanced equation for this reaction.
 - (b) What is the oxidizing agent?

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- (c) What is the reducing agent?
- (d) What are the other metals in the same group as Beryllium?
12. Determine the symmetry element(s) for (5%)
(a) an s orbital (b) a d_{xy} orbital (c) CO_3^{2-} (d) SF_4 (e) NH_2Cl
13. Give the formula and name of a molecule, a molecular ion or solid that is
isoelectronic and isostructural with (5%)
(a) NH_3 (b) Si (c) N_2 (d) N_2O_4 (e) nitrate ion