

國立清華大學 命題紙

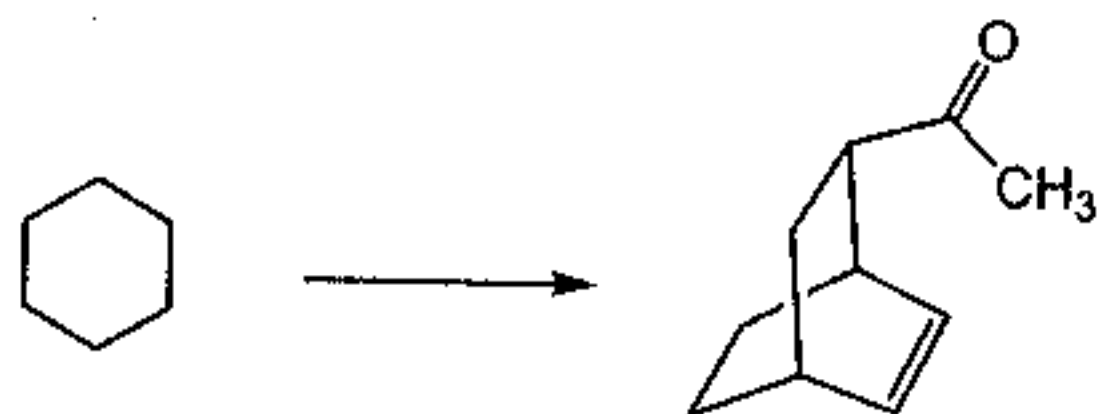
九十二學年度 化學系(所) 化學、應用化學 組碩士班研究生招生考試
科目_無機化學及有機化學_科號_0602, 0702_共_5_頁第_1_頁 *請在試卷【答案卷】內作答

1. The Fe=O oxidizing center in P-450 is characterized as an Fe(IV) complex with the porphyrin also oxidized by one electron. Such a picture receives strong support from the ^{57}Fe Mössbauer spectrum of the species. The complex has a magnetic susceptibility that indicates the presence of three unpaired electrons. To what orbitals are they assigned? (5%)
2. A highly successful commercial process to produce acetic acid is based on the rhodium-catalyzed carbonylation of methanol, the Monsanto process. Describe the proposed mechanism for the conversion of methanol and CO to acetic acid. (5%)
3. Propose a set of reactions for the formation of $\text{W}(\text{CO})_5(\text{C}(\text{OCH}_3)\text{Ph})$, starting with hexacarbonyltungsten(0) and other reagents of your choice. (5%)
4. Explain the CO binding to transition metal to form M-CO complex instead of M-OC by utilizing MO theory, i.e. draw the CO molecular orbital scheme to explain your answer. (5%)
5. The redox reactions are classified into the inner-sphere mechanism and the outer-sphere mechanism. Define these two terms by examples, individually. (5%)
6. Predict the probable products of the following reactions, and write the balanced chemical equations. (10%)
 - (a) BF_3 and excess NaF in acidic aqueous solution.
 - (b) BCl_3 and excess NaCl in acidic aqueous solution.
 - (c) BBr_3 and excess $\text{NH}(\text{CH}_3)_2$ in a hydrocarbon solvent.
7. Observations on a complex in which HD replaces H_2 were used to show that H_2 is bound in $[\text{W}(\text{CO})_3(\text{P}^t\text{Pr}_3)_2(\text{H}_2)]$ without H-H bond rupture (*JACS*, 1984, 106, 451). If the dihydrogen complex has an H-H stretch at 2695 cm^{-1} , what would be the expected wavenumber of the HD complex? What should be the pattern of the ^1H -NMR signal arising from coupling with D in the HD complex? (10%)
8. The magnetic moment of an octahedral Co(II) complex is $4.0\ \mu_{\text{B}}$. What is its electron configuration? (5%)
9. Using the given starting material and any necessary reagent(s) to complete each of the following

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transformations. Show all synthetic intermediate(s). (12%)

(a)

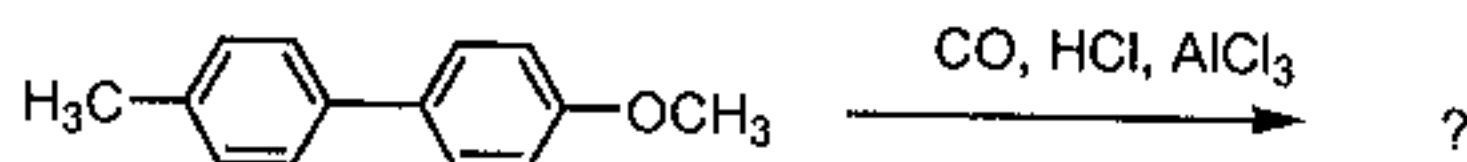


(b)

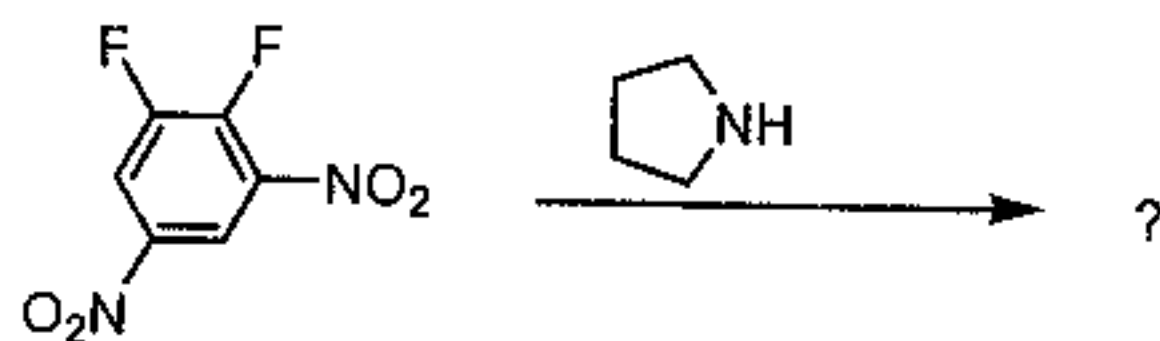


10. Predict the structure, including stereochemistry when necessary, of the major reaction product or provide necessary reagent(s) for each of the following reactions. (15%)

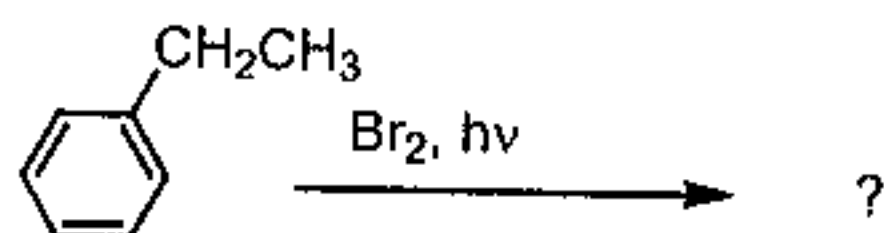
(a)



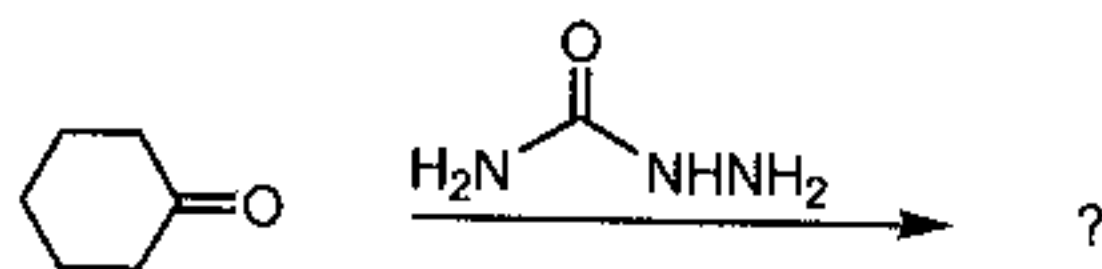
(b)



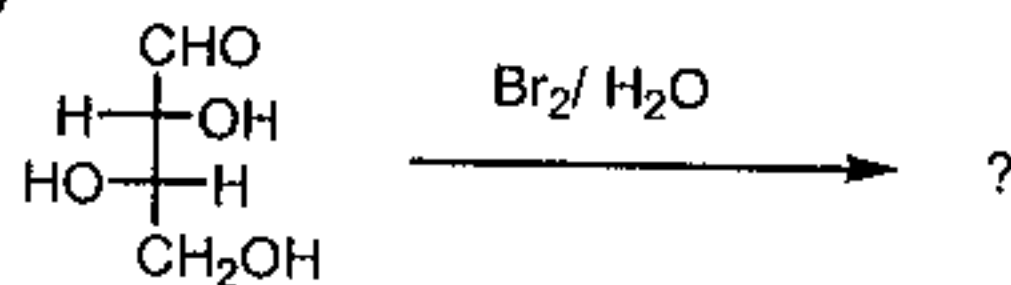
(c)



(d)

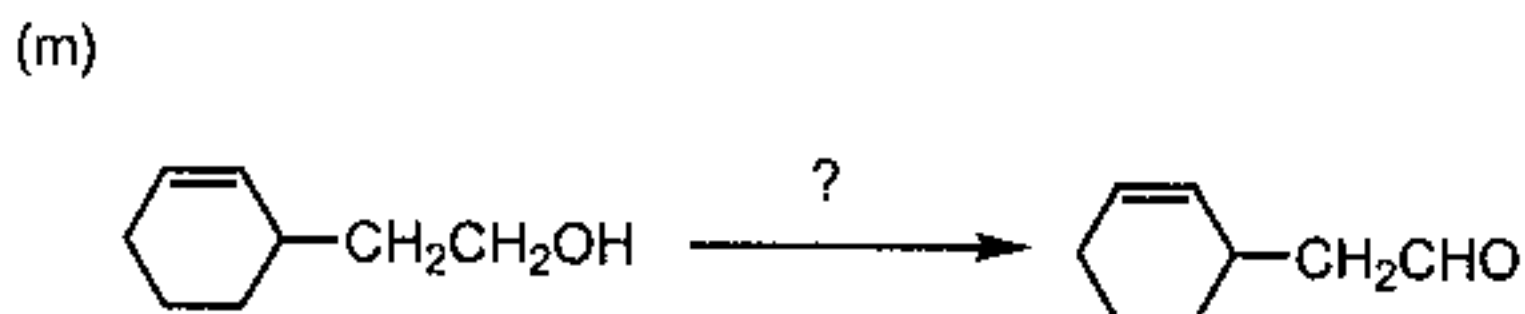
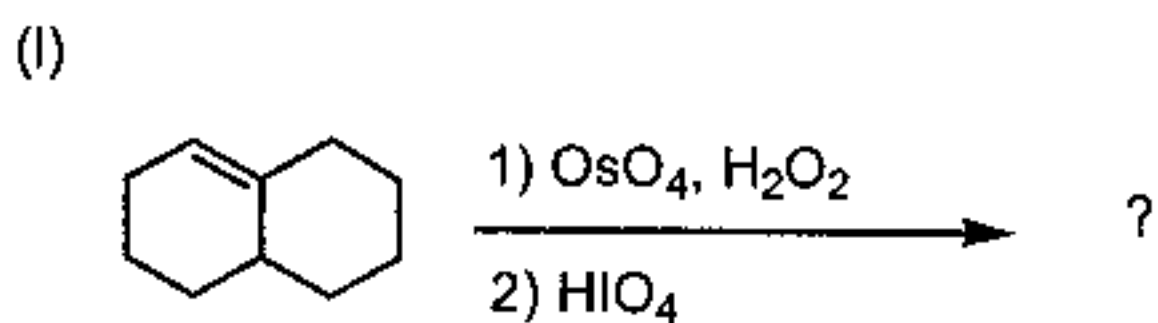
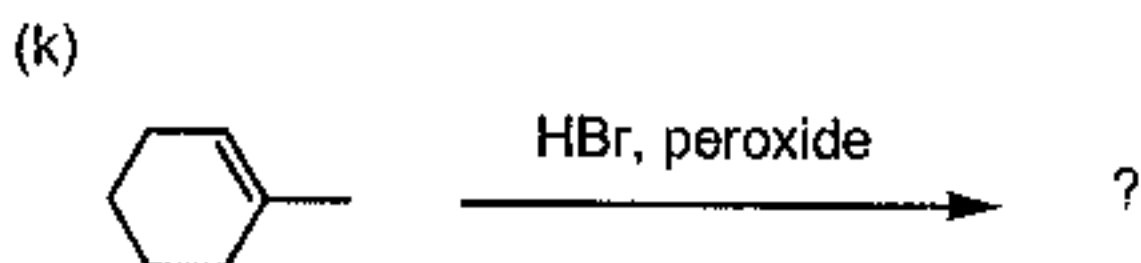
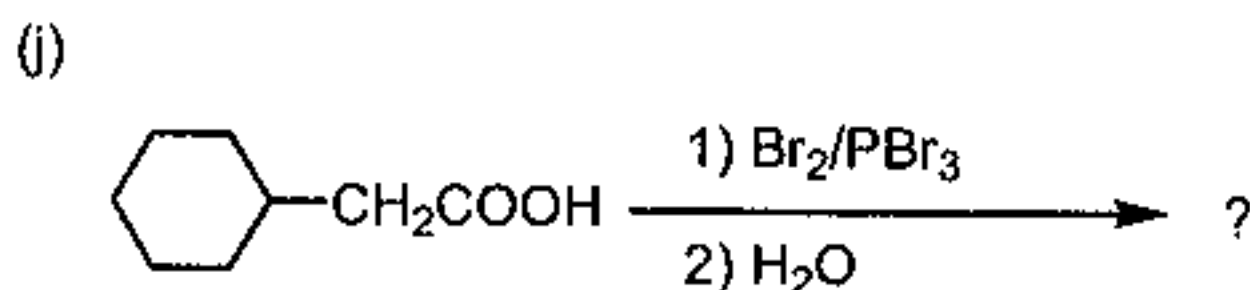
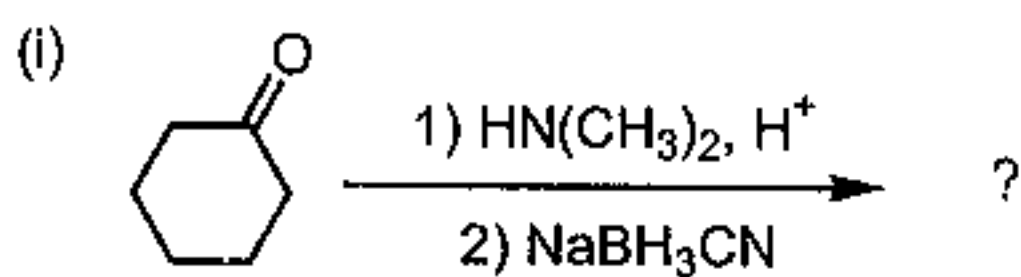
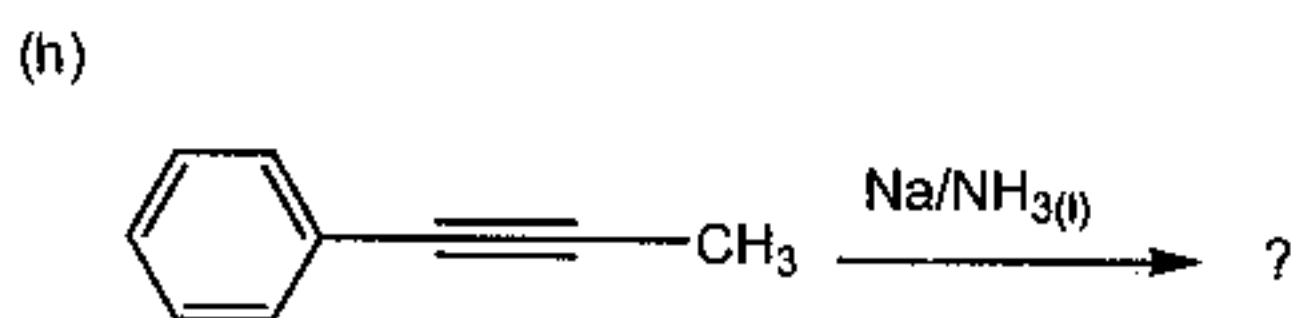
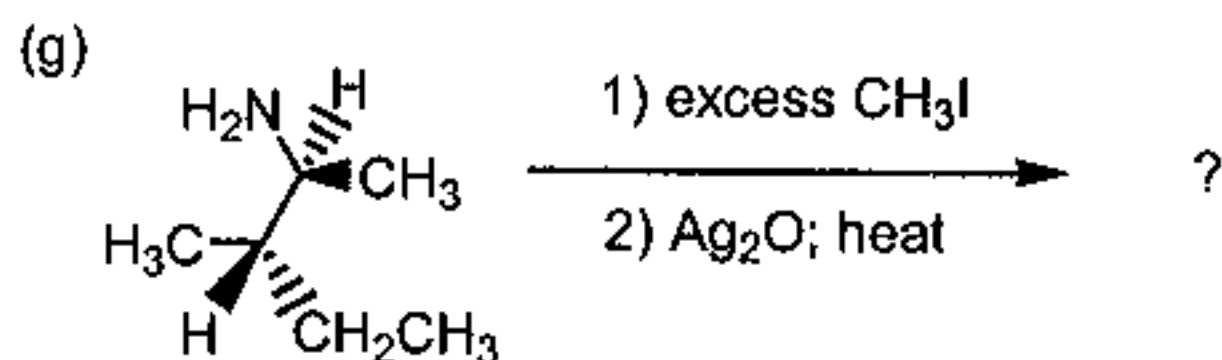
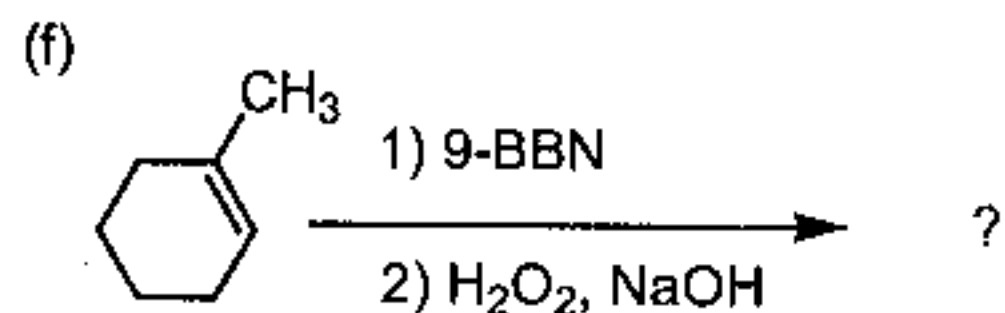


(e)

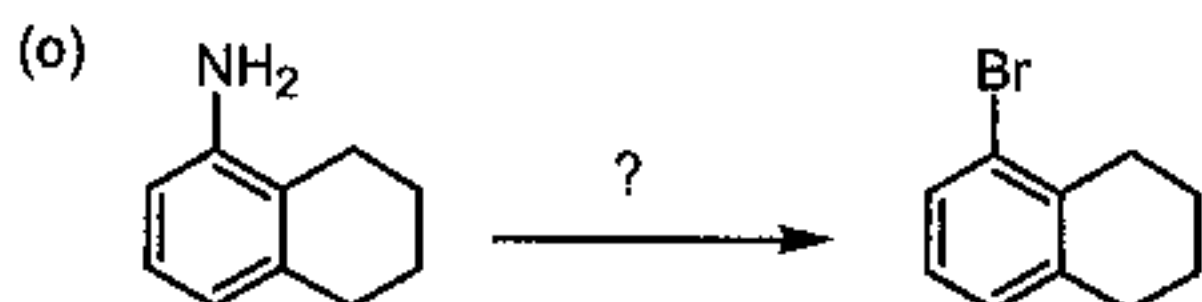
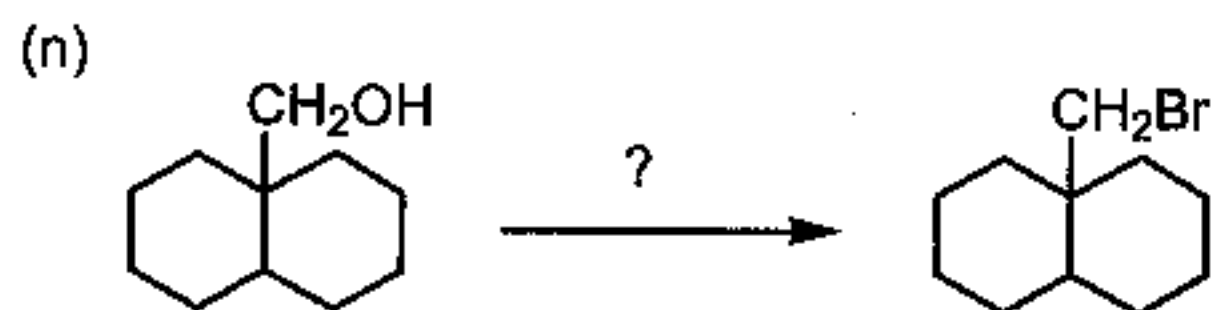


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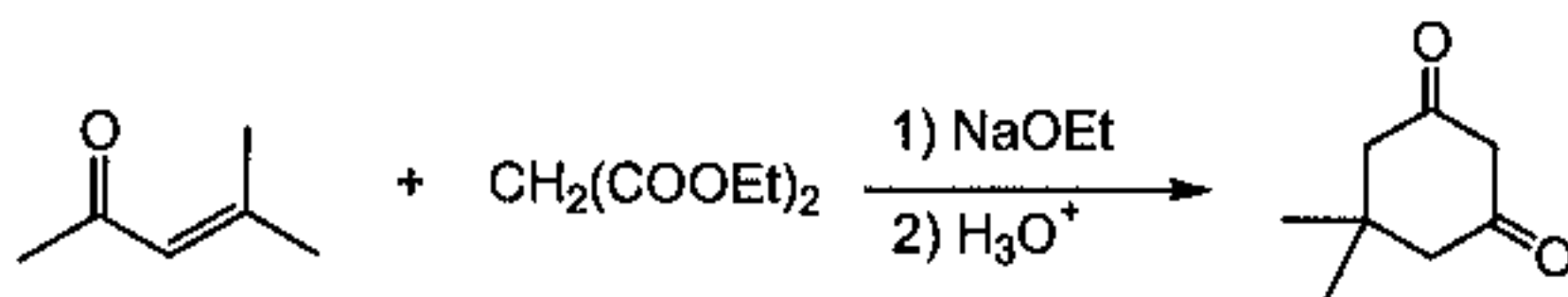


11. Show simple chemical test(s) that would allow one to distinguish the compounds in each of the following sets. (8%)

(a) 2-pentanol, 3-pentanol, 2-methyl-2-pentanol

(b) 1-hexyne, 2-hexyne, 2-hexanone

12. Propose a plausible reaction mechanism for the following transformation. (5%)



13. Deduce the molecular structure for the compound that is consistent with the following spectral data. (10%)

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