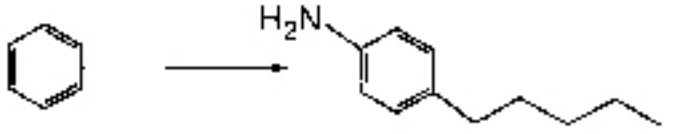
八十六學年度輻射生物研究所系（所）＿＿＿＿組碩士班研究生入學考試

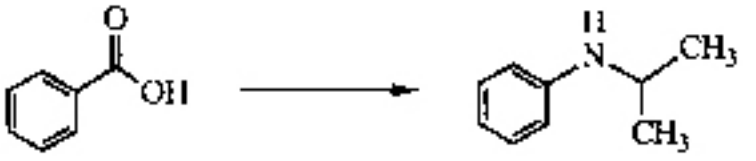
科目＿有機化學＿＿科號 4103 共 5 頁第 1 頁 *請在試卷【答案卷】內作答

1. Show how you would accomplish the following synthetic transformations, and provide all intermediates. (20%)

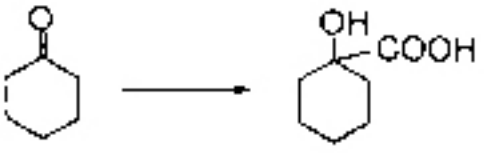
(a)



(b)

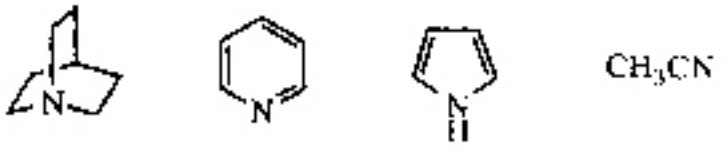


(c)

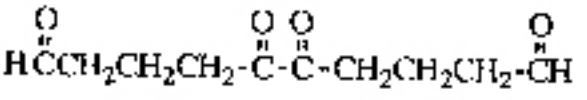


(d)

2. Rank the following amines in an order of increasing basicity, and give your reason for the arrangement.(3%)



3. Hydrocarbon **A**, $C_{10}H_{14}$, has an ultraviolet absorption at λ_{max} = 236nm and gives hydrocarbon **B**, $C_{10}H_{18}$, on catalytic hydrogenation. Ozonolysis of **A** followed by zinc/acetic acid treatment yields the following diketo dialdehyde:



(a) Hydrocarbon **A** reacts with maleic anhydride to yield a Diels-Alder adduct. Propose a molecular structures for **A**.

(b) What is the structure of the Diels-Alder adduct? Clearly indicate the stereochemistry of the adduct where appropriate.(5%)

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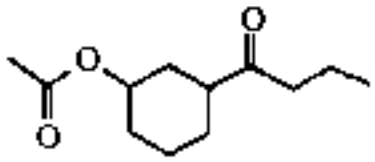
4. Draw the totally eclipsed, ecliped, gauch, aud anti conformations for 1,2-ethanediol. Which conformation is the most stable one? explain.(4%)

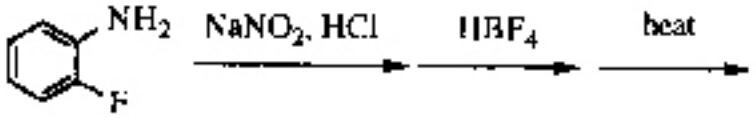
5. Give the structure of the major product you would expect for each of the following reactions, and clearly indicate the stereochemistry of the product where appropriate. (40%)

(a) 2-pentyne + Na, liquid ammonia ⟶

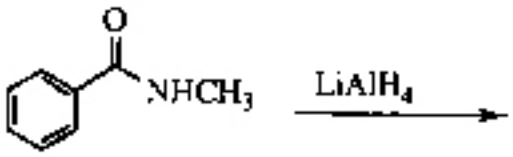
(b)



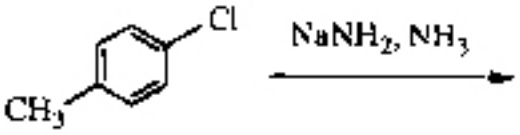
(c)



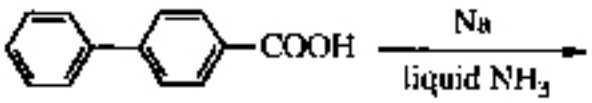
(d)



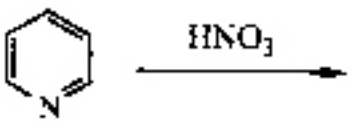
(e)



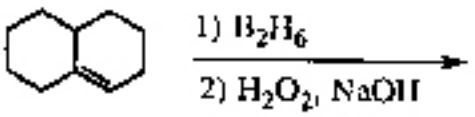
(f)



(g)



(h)



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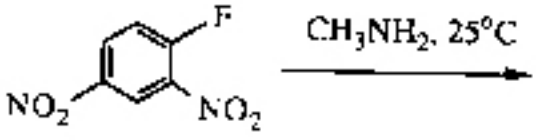
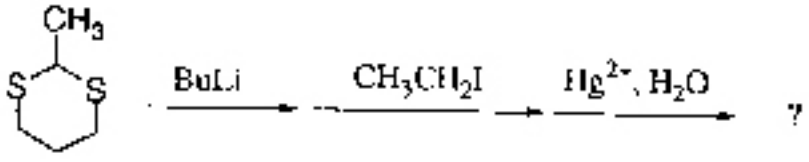
(i)

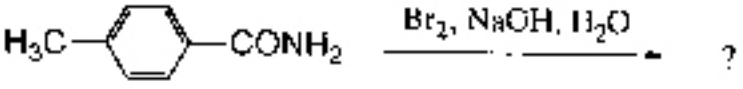


(j) 1,2-epoxyhexane + H^+, CH_3OH ⟶

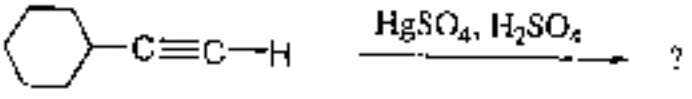
(k)



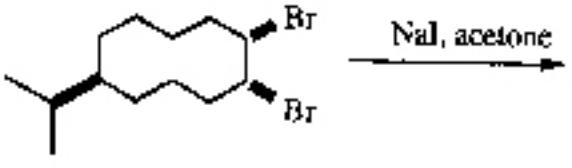
(l)



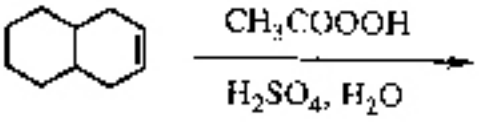
(m)



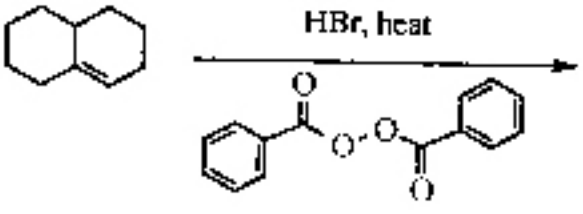
(n)



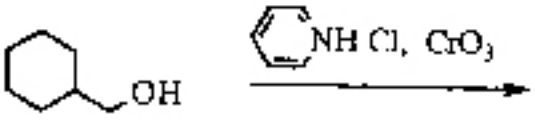
(o)



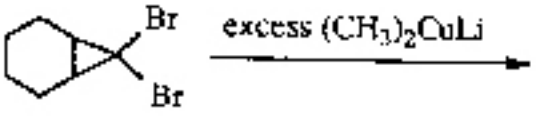
(p)



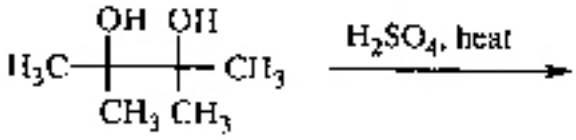
(q)



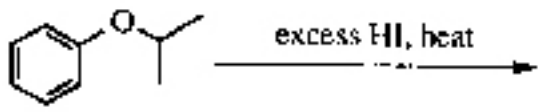
(r)



(s)



(t)



6. Reaction of 2,3-dimethyl-1,3-butadiene with Cl_2 in carbon tetrachloride in the dark at -20°C gives 45% of expected product, 1,4-dichloro-2,3-dimethyl-2-butene, in addition to 54% of **C** and 1% of **D**.

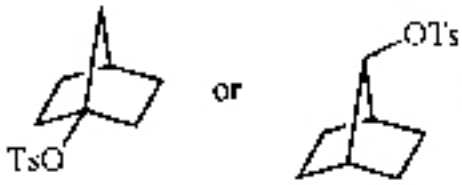
Compound **C** shows mass spectral parent peaks at m/z 118 and 116, with an intense fragment peak at m/z 81. The NMR spectrum shows singlets at δ 1.90(3H), 4.20(2H), and four peaks at δ 6.06, 6.19, 6.22, and 6.30(4H).

Compound **D** also shows mass spectral parent peaks at m/z 118 and 116. The NMR spectrum shows singlets at δ 1.78(3H), 1.85(3H), 6.20(1H), and two peaks at δ 5.08, 5.0(2H).

Deduce the structures of **C** and **D** and write a plausible mechanism for their formations.(10%)

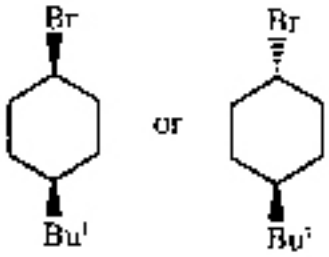
7. For the following pairs of reactions indicate which you would expect to be more favorable and explain the basis of your prediction.(6%)

(a) Which compound would be expected to react faster?



when treated with hot acetic acid

(b) Which compound would be expected to react faster?



when reacted with KOBu^t

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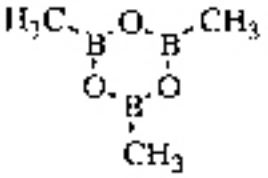
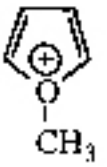
8. Show how you would use extractions with a separatory funnel to separate a mixture of the following compounds.(4%)

benzoic acid　　phenol　　benzyl alcohol　　aniline

9. Classify each of the following molecules and ion as aromatic, antiaromatic, or nonaromatic species.(3%)





10. An unknown compound (C_3H_2NCl) shows moderately strong IR absorbions around 1650 cm^{-1} and 2200 cm^{-1}. Its NMR spectrum consists of two doublets (J = 14 Hz) at d 5.9 and d 7.1. Deduce a structure consistent with these data. (5%)