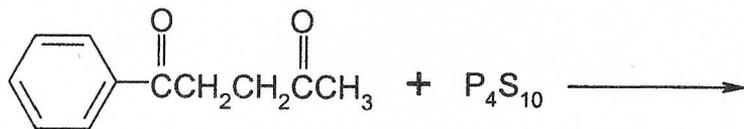
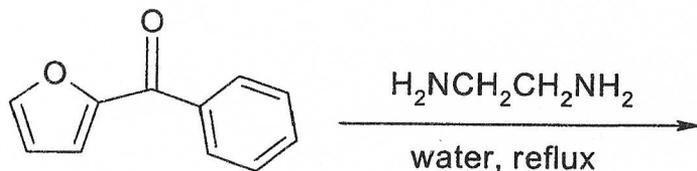


1. Predict the structure, including stereochemistry when necessary, of the major reaction products for each of the following reactions. (20 %)

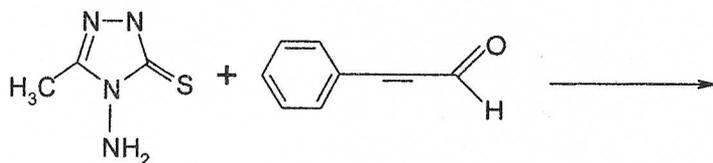
(A)



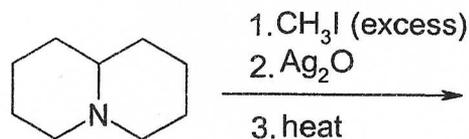
(B)



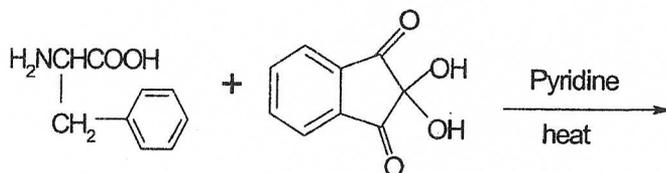
(C)



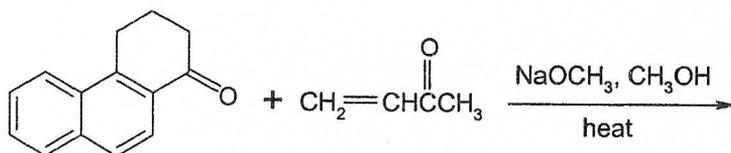
(D)



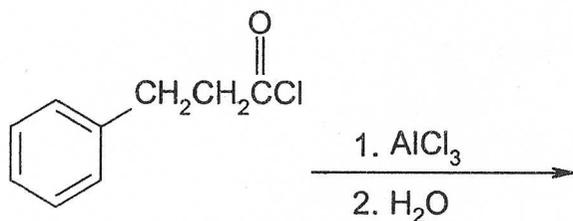
(E)



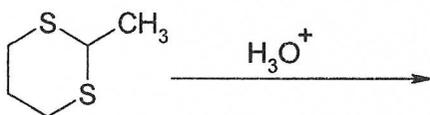
(F)



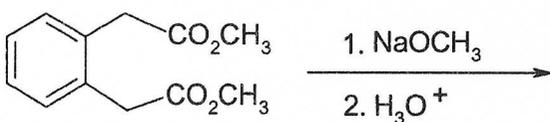
(G)



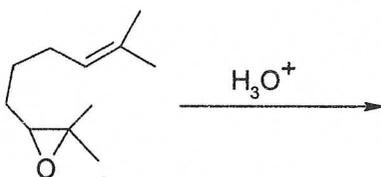
(H)



(I)

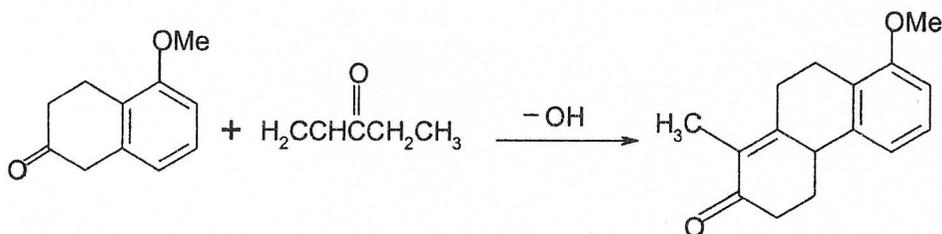


(J)

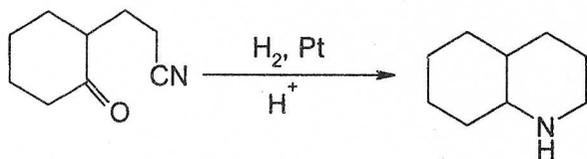


2. Please provide a detailed, step-by-step mechanism for the following reactions. (24%)

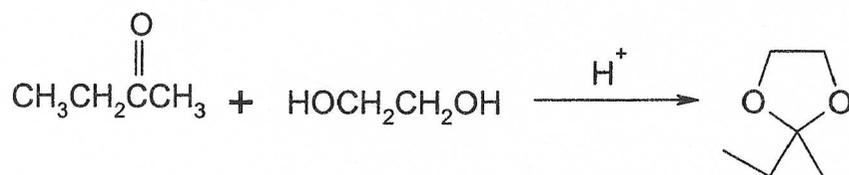
(A)



(B)

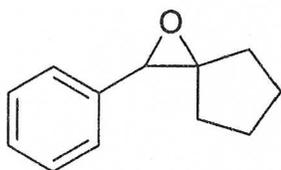


(C)

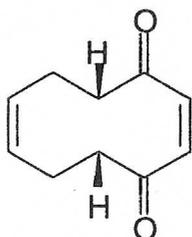


3. Show how you would synthesize the following compounds from starting materials listed below (20%)

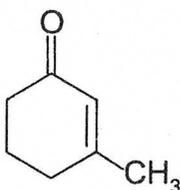
(A) Using starting materials contain no more than six carbon atoms.



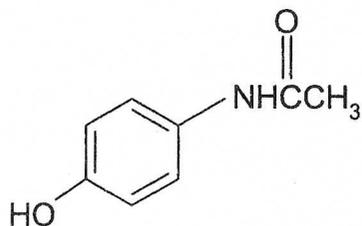
(B) Using Diels-Alder reactions.



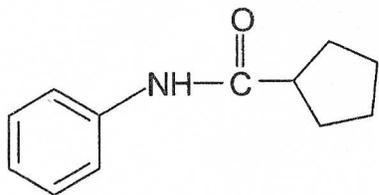
(C) Using acetoacetic ester synthesis.



(D) Using phenol as the starting material



(E) Using benzene as the starting material.



4. Fullerenes (C_{60}) was first discovered by Kroto, Smalley and Curl in 1985, and has become a widely used nanomaterial nowadays. It only contains five- and six-membered rings. The bond lengths that are shared by five- and six-membered rings are 1.45 and 1.39 Å, respectively. Because of its curvature, the energy content of the constituent benzene rings is about 10.16 kcal/g C atom. According to these information, please answer the following questions: (8 %)

- (A) How many five- and six-membered rings are contained in a fullerenes.
 (B) Use the bond length and energy content to predict the possible reactions of a fullerenes.
 (C) Predict the ^{13}C NMR and FTIR spectra.
 (D) Predict its solubility in protic and aprotic solvents (e.g. water, ethanol, THF, acetone)

5. Deduce the identity of the following compounds from the spectral data given: (8 %)

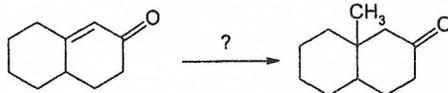
- (A) $C_5H_{10}O$: 1H NMR: δ 1.2 (6H, doublet), 2.1 (3H, singlet), 2.8 (1H, septet) (ppm)
 IR: 2980, 1710 cm^{-1}
 MS: m/z 71, 43
- (B) $C_4H_6O_2$: 1H NMR: δ 2.28 (2H, multiplet), 2.50 (2H, triplet), 4.35 (2H, triplet) (ppm)
 ^{13}C NMR: δ 177.81 (singlet), 68.58 (triplet), 27.70 (triplet), 22.17 (triplet) (ppm).

6. Multiple choices (20 %).

(A) Among the butane conformers, which occur at energy minima on a graph of potential energy versus dihedral angle?

- (1) gauche only (2) eclipsed and total eclipsed (3) gauche and anti
 (4) eclipsed only (5) anti only

(B) What reagents would you use to accomplish the following conversion?



- (1) CH_3Br, H_3O^+ (2) CH_3MgBr, H_3O^+ (3) $(CH_3)_2CuLi, H_3O^+$
 (4) $CH_3Br, LiAlH_4, H_3O^+$ (5) $LiAlH_4, CH_3MgBr, H_3O^+$

(C) When pyridine is treated with a mixture of nitric and sulfuric acids, the major product is

- (1) 2-nitropyridine (2) 3-nitropyridine (3) 4-nitropyridine
 (4) 3-aminopyridine (5) 4-aminopyridine

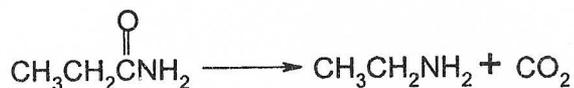
(D) When 1,3-cyclopentadiene reacts with the *cis*-isomer of $\text{NCCH}=\text{CHCN}$, the major product is

- (1) optically active
 (2) a meso compound
 (3) a racemic mixture
 (4) a spirocyclic compound
 (5) a fused bicyclic compound

(E) The transformation of 4-methylbenzenediazonium bromide to toluene is best carried out by using

- (1) H^+ , H_2O (2) H_3PO_2 , H_2O (3) H_2O , OH^-
 (4) Zn , NaOH (5) H_2SO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$

(F) Identify the best conditions for the following transformation



- (1) H_2 , metal catalyst (2) excess CH_3I , K_2CO_3 (3) Br_2 , NaOH , H_2O
 (4) LiAlH_4 , ether (5) CH_2N_2 , ether

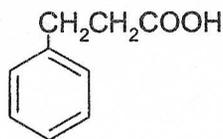
(G) In the UV-visible spectrum of (E)-1,3,5-hexatriene, the lowest energy absorption corresponds to

- (1) a σ to π transition (2) a σ to π^* transition (3) a π to σ^* transition
 (4) a σ to σ^* transition (5) a π to π^* transition

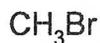
(H) *p*-Methoxybenzaldehyde can be prepared from anisole using the Gatterman-Koch formylation. What mixture of reagents is necessary for this process?

- (1) CO , HCl , AlCl_3 , CuCl
 (2) CO , SO_3 , H_2SO_4
 (3) CO_2 , HCl , AlCl_3
 (4) CO_2 , SO_3 , H_2SO_4
 (5) CO_2 , HNO_3 , H_2SO_4

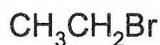
(I) What alkyl bromide should be used in the malonic ester synthesis of the following carboxylic acid?



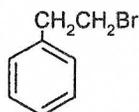
(1)



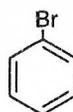
(2)



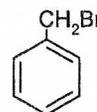
(3)



(4)

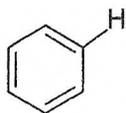


(5)



(J) Which of the following carbon-hydrogen bonds exhibits the lowest wavenumber for a C-H stretch in infrared spectroscopy?

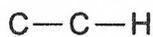
(1)



(2)



(3)



(4)



(5)

