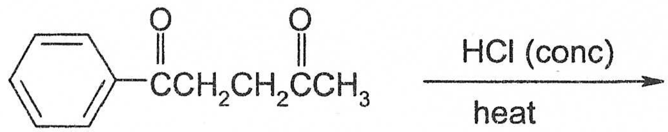
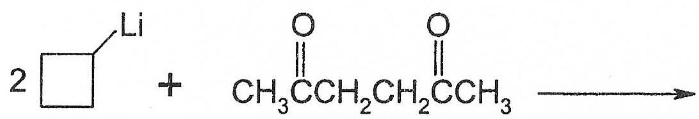
1. Predict the structure, including stereochemistry when necessary, of the major reaction products for each of the following reactions. (30 %)

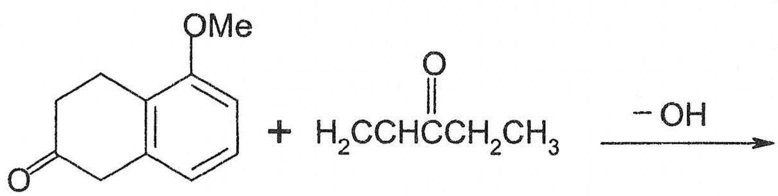
(A)



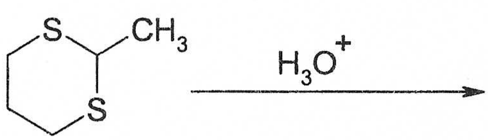
(B)



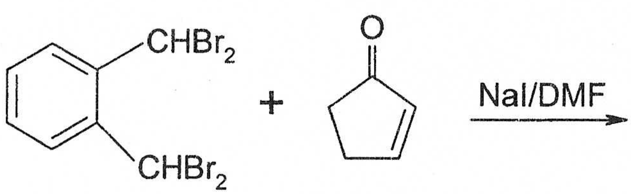
(C)



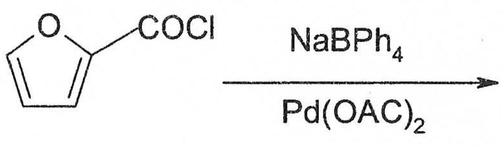
(D)



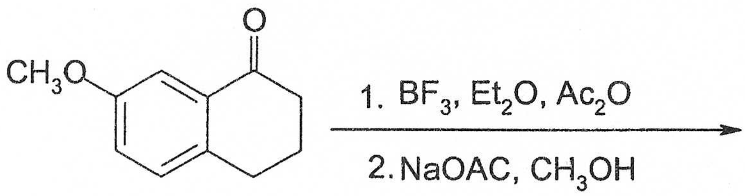
(E)



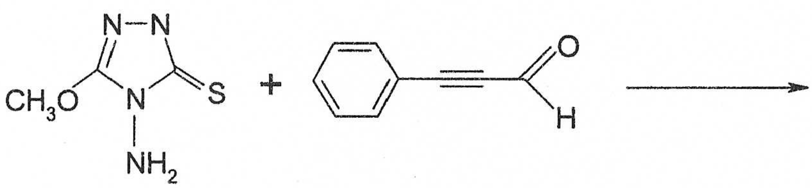
(F)



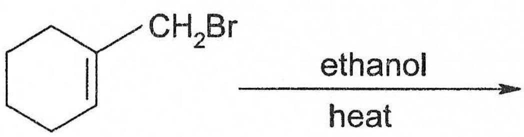
(G)


CH3O
O
1. BF3, Et2O, Ac2O
2. NaOAC, CH3OH

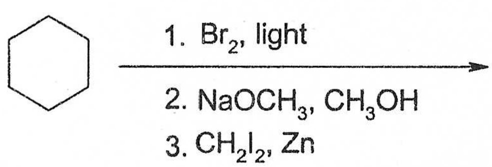
(H)


N−N
CH3O
N
S
NH2
+
O
H

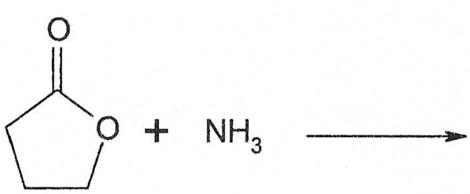
(I)


CH2Br
ethanol
heat

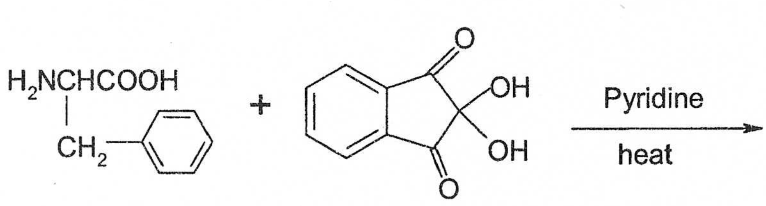
(J)


1. Br2, light
2. NaOCH3, CH3OH
3. CH2I2, Zn

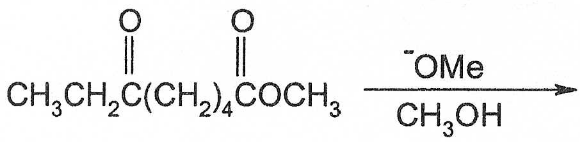
(K)


O
O
+ NH3

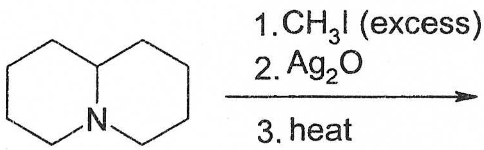
(L)


H2NCHCOOH
CH2
+
O
OH
OH
O
Pyridine
heat

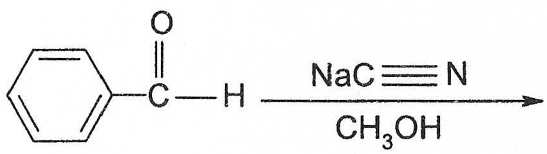
(M)



(N)



(O)



2. 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: (10 %)

(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.

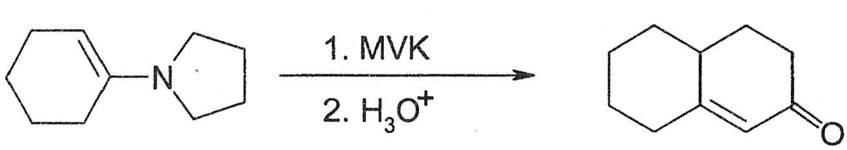
(c) Predict the ^{13}C NMR and FTIR spectra.

(d) Predict its solubility in protic and aprotic solvents (e.g. water, ethanol, THF, acetone).

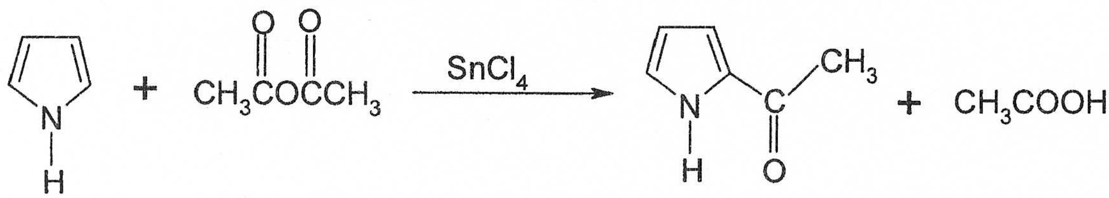
(e) Is that possible to produce C_{60} in the natural environment?

3. Please provide a detailed, step-by-step mechanism for the reactions list below (24 %)

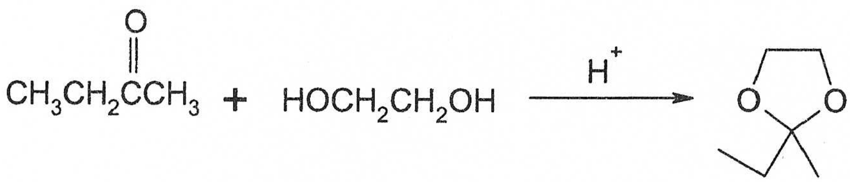
(A)



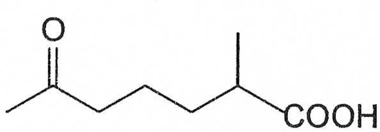
(B)



(C)



4. Compound D, formula $C_8H_{14}O$, is converted by $CH_2{=}P(C_6H_5)_3$ into compound E, C_9H_{16}. Treatment of compound D with $LiAlH_4$ yields two isothermic products F and G, both $C_8H_{16}O$, in unequal yield. Heating either F or G with concentrated sulfuric acid produces compound H, with the formula C_8H_{14}. Ozonlysis of H produces a keto aldehyde after Zn-H^+, H_2O treatment. Oxidation of this keto aldehyde with aqueous Cr(VI) produces the compound list below. Please identify compounds D through H. Pay attention to the stereochemistry of D. (10%)



5. Deduce the identity of the following compounds from the spectral data given (10 %).

(A) $C_7H_{10}O_2$: ^{1}H NMR: δ 1.16 (3H, singlet), 2,21 (2H, singlet) (ppm)

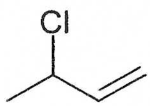
^{13}C NMR: δ, 216.25 (signet), 52.57 (singlet), 34.51 (triplet), 20.22 (quartet) (ppm).

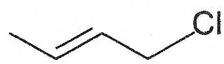
(B) $C_9H_{10}O_2$: ^{13}C NMR: δ 18.06 (quartet), 45.40 (doublet), 127.32 (doublet), 127.55(doublet), 128.61 (doublet), 139.70 (singlet) (ppm)

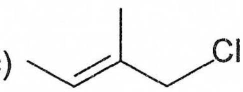
IR: broad 3500-2800, 1708 cm^{-1}.

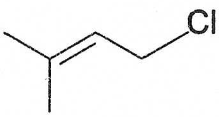
6. Consider the possible thermal [4+4] cycloaddition of two molecules of 1,3-butadiene to generate cycloocta-1,5-diene. Show the HOMO/LUMO interaction which would result, and use this interaction to predict whether the proposed cycloaddition could occur. (6 %)

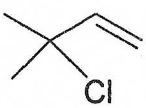
7. (A) Rank the following six molecules in order of decreasing S_N1 reactivity and decreasing S_N2 reactivity. (5%)

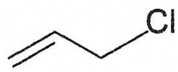
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

(B) How would you expect the S_N2 reactivities of simple saturated primary, secondary, and tertiary chloroakanes to compare with the S_N2 reactivities of the compounds list above? Make the same comparison for S_N1 reactivity also (5%).