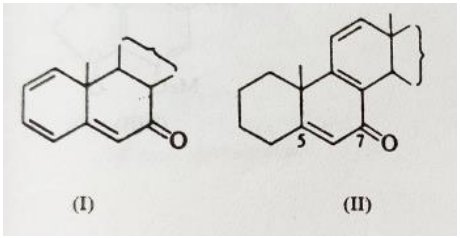
Organic Spectroscopy

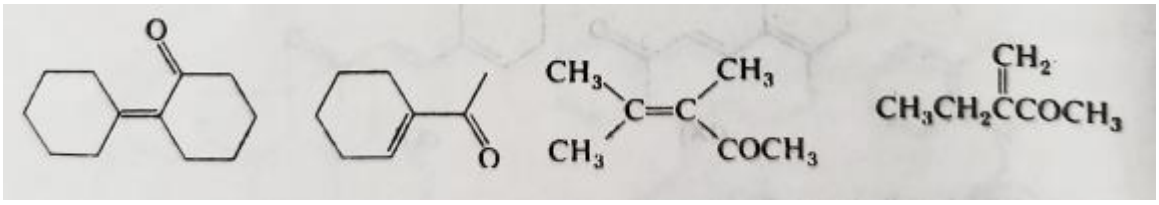
1. On the basis of Woodward rules, calculate the expected position of the absorption maximum in the following compounds. How you compare the calculated value with the observed value of λ_{max} 230 nm (€ 18000); 278 nm (€ 3720) and 348 nm (€ 11000) in case of I;
   λ_{max} 256 nm and 327 nm in case of II.



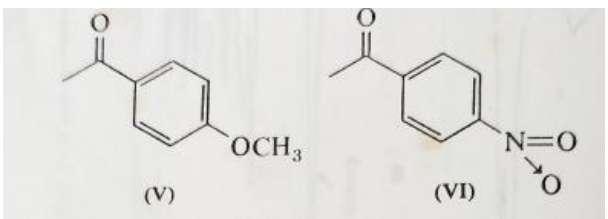
2. Which structural features produce a bathochromic or hypsochromic effect in an organic compound?
3. Aniline absorbs at 230 nm (€ 8600); however in acid solution, the main absorption band is seen at 203 nm (€ 7500) and is comparable with benzene. Explain.
4. The position of absorption bands of acetone shifts in different solvents: 279 nm in hexane, 272nm in ethanol and 265 in water. Explain.
5. Distinguish between the following compounds by UV spectroscopy :

(i) 2,6,N,N-tetramethylaniline and 3,5,N,N-tetramethylaniline
(ii) Phenol and 4-nitrophenol
(iii) 2-nitroaniline and 4- nitroaniline
(iv) Cis- stilbene and trans-stilbene

6. The labels fell off from the four bottles of ketones which have the structures shown below, the absorption bands in uv spectra of them are given as : λ_{max} at 221, 249, 233 and 258 nm. Assign structures to them.



7. Which of the compounds (V and VI) is expected to show a lower C=O frequency in IR spectrum and why?



8. Distinguish between the following compounds by IR spectroscopy.

(i) Toluene and trideuteriomethyl benzene

(ii) *Meso*- and *dl*-butane 2,3-diol

(iii) Cyclopentanone, cyclohexanone and cyclohexenone

(iv) Cyclohexanone, cyclopentanecarboxaldehyde and 2-methylcyclopentanone

(v) $Me_2CHCOCH_2COCH_3$ and $CH_3COCMe_2COCH_3$

(vi) $CH_3COOCH=CH_2$ and $H_2C=CHCOOCH_3$

9. The C=C stretching frequency of 2-Methylpropene in IR absorption is shown to be 1640cm^{-1}, whereas, no absorption peak appears in that region for 2,3-Dimethyl-2-butene.Explain.

10. A concentrated solution of ethanol in CCl_4 and ethylene glycol exhibit a broad band in IR spectrum near 3350 cm^{-1}. On dilution with CCl_4, the spectrum of ethylene glycol does not change, but that of ethanol shows a sharp band at 3600 cm^{-1} in addition to the broad band at 3350 cm^{-1}. Explain.

11. Ethyl acetoacetate shows the peaks at 1715 cm^{-1} ,1690 cm^{-1} , 2900 cm^{-1} and 3500 cm^{-1} in IR spectrum. How will you justify it?

12. Why do primary amides show two N—H bands, while secondary amides show only one in their IR spectrum?

13. Give the characteristic absorption bands in the IR spectrum of PHCHO. What changes will you observe in the absorption bands if PhCHO is oxidised to PhCOOH?

14. Treatment of 2-Methylcyclohexanone with a ketone [A], C_4H_6O, in presence of a base followed by acidification gave [B], $C_{11}H_{16}O$, which shows λ_{max} 244 nm (€ 10000) in its UV spectrum and carbonyl stretching at 1640 cm^{-1} in its IR spectrum. Explain the reaction and the spectral data of compound [B].

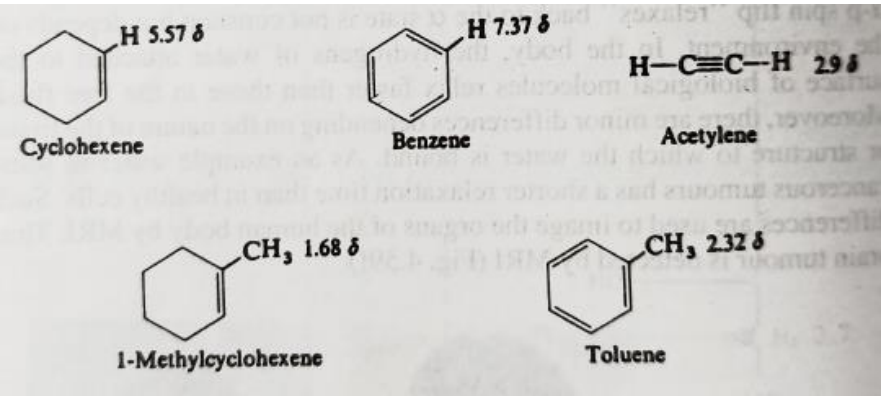
15. Which of the following atoms do not show nuclear magnetic resonance?

^{12}C , ^{16}O , ^{14}N , ^{19}F , ^{32}S

16. Sketch and explain the ^{1}HNMR spectrum of m-dinitrobenzene, o-dichlorobenzene showing the relative chemical shifts. State the splitting pattern of the signals.

17. Sketch the ^{1}HNMR spectrum with integrations showing the relative chemical shifts of isomeric dibromoethanes.

18. How do you explain the chemical shift data of the following compounds?



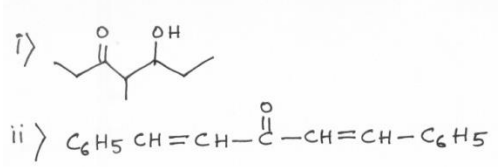
19. Why TMS is used as reference compound ^{1}HNMR?

A compound having molecular formula $C_6H_{10}O$ shows a 6H singlet at 2.3 ppm, a 1H singlet at 6.09 ppm and a 3H singlet at 2.27 ppm in the ^{1}HNMR spectra. The compound shows UV absorption

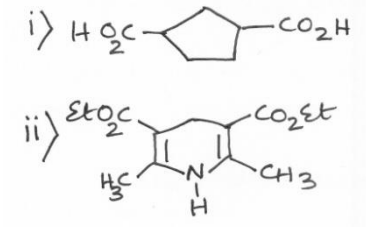
at λ_{max} 230 nm and 329 nm in hexane. Identify the structure of the compound with proper assignment of the ^{1}HNMR signals.

The Logic of Organic Synthesis

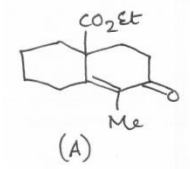
1. Work backward to identify the starting materials which, upon aldol condensation, produce the following compounds. (4)



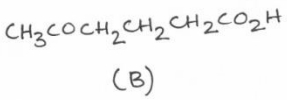
2. Work backward to derive suitable readily available starting material for the synthesis of the following compounds and then retrace the steps forward: (4)



3. Apply acyloin condensation reaction for the synthesis of a 4-membered ring. (2)
4. How would you prepare compounds (A) and (B), where at least one step of the reaction sequence is a Michael addition in each case? (4)

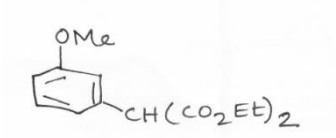


(A)

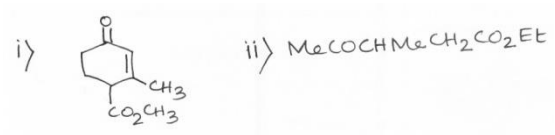


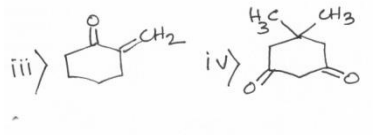
(B)

5. Write down any suitable synthesis of the following compound: (2)



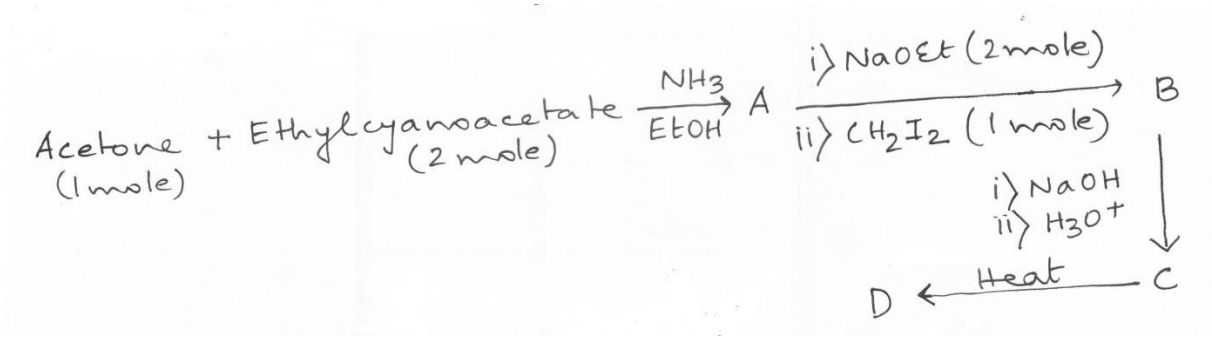
6. Synthesize the following compounds from suitable starting materials. (3 each)



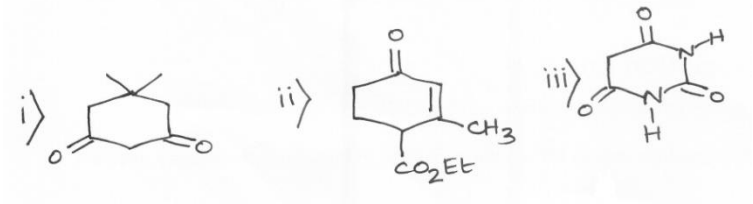


7. Work backwards to devise synthetic route to the following target molecules. (2 each)

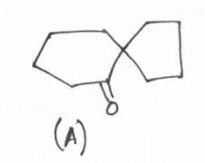
8. Identify the products A-D in the following reaction sequence (mechanism not required) (4)



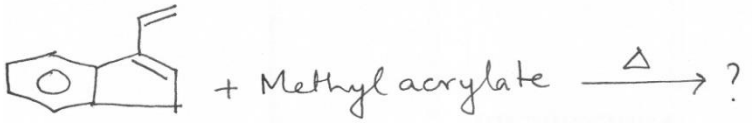
9. Define the following terms with examples: (2 each)
   i) Functional Group Interconversion ii) Functional Group Addition iii) Stereospecific Reaction
10. Describe the synthesis of the following compounds with proper retrosynthetic analysis. (3 each)



11. Outline the synthesis of the compound (A) from diethyl adipate. Give mechanisms of the steps involved. (5)

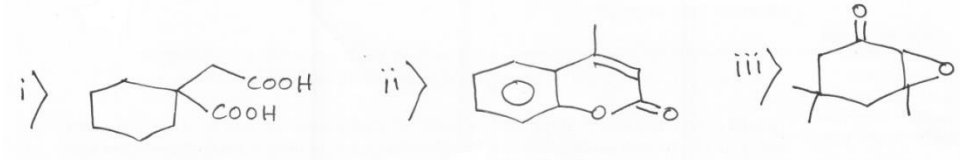


12. Predict the product of the following reactions and justify. (3)

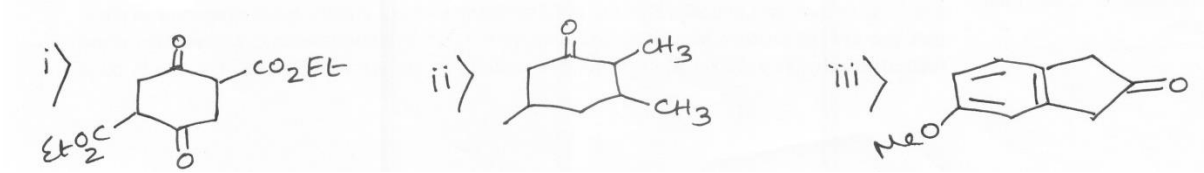


13. Using Claisen ester condensation reaction, how would you prepare the following compounds. (3 each)

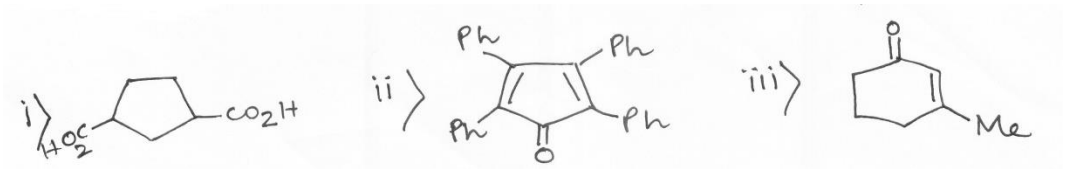
14. How can you synthesize the following compounds. (3 each)



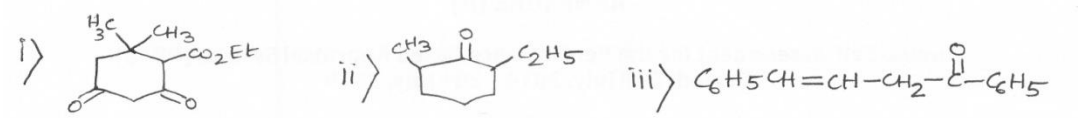
15. Describe the synthesis of the following compounds with proper retrosynthetic analysis. (3 each)



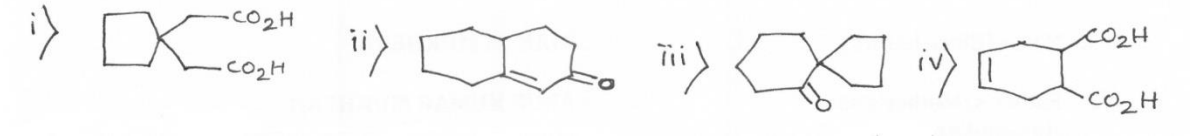
16. How can you synthesize the following compounds from readily available starting materials. (3 each)



17. Work backward to formulate a scheme for the synthesis of 4-methoxyacetanilide using Beckmann rearrangement as one of the steps in your scheme. (4)
18. Suggest suitable method for the synthesis of 5,5-dimethylcyclohex-1,3-dione using Michael condensation. (4)
19. Explain with proper example the meaning of the term "Synthon" (1)
20. Describe the synthesis of the following compounds with proper retrosynthetic analysis. (3 each)

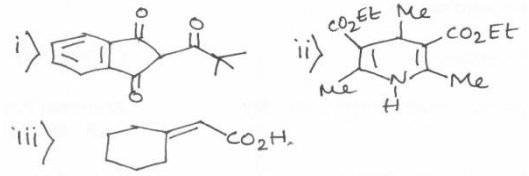


21. How would you prepare the following compounds: (2 each)
    i) 2-Methylcyclopentane from diethyladipate
    ii) 2,2,6,6-Tetramethyl-4-pipyridone from acetone.
22. Write down the synthesis of the following compounds: (2 each)

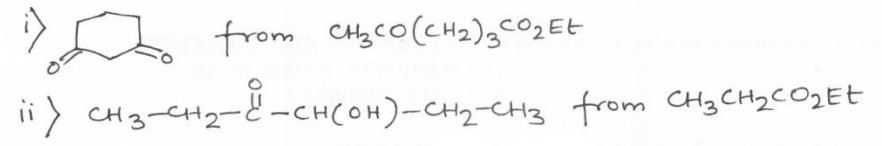


23. Trace out a feasible retrosynthetic pathway for the synthesis of the following compound: (2)

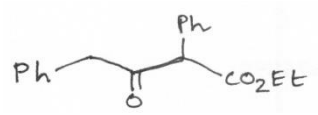
24. Explain with proper examples the meaning of the terms 'umpolung', 'illogical electrophile' and 'illogical nucleophile'. (3)
25. Describe the synthesis of the following compounds with proper retrosynthetic analysis. (2 each)



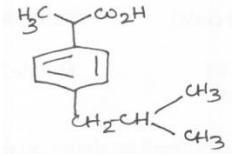
26. Illustrate the meaning of the following terms with example:
    i) Regioselective synthesis ii) Stereoselective synthesis
27. How would you prepare the following compounds: (2 each)



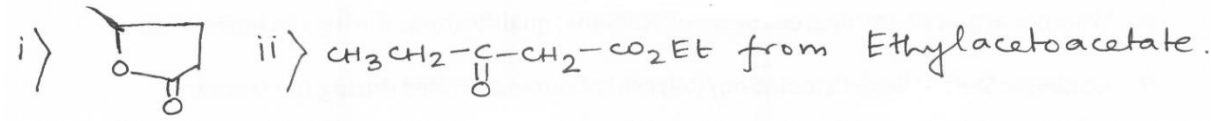
28. Explain the term 'synthetic equivalent' with suitable chemical reaction. (2)
29. Discuss two different retrosynthetic pathways for the following compound. Which pathway will lead to the efficient synthesis of the target molecule and why? (4)



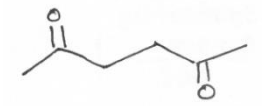
30. Outline the synthesis of the following compound from benzene. (2)



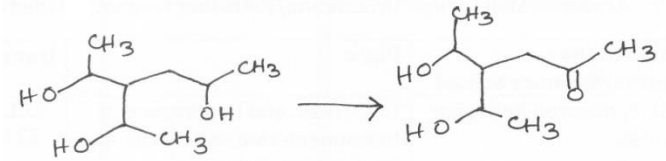
31. How can you synthesize the following compounds. (3 each)



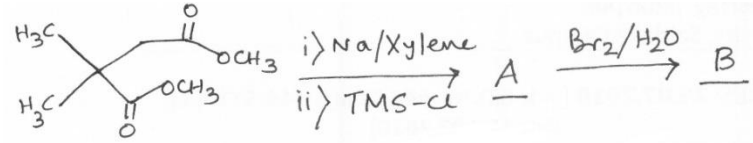
32. What is chemoselective reaction. Give an example. (2)
33. Write the retrosynthesis of the following compound in two different ways:
    Give one synthetic method for the preparation of the above compound. What happens when this compound is treated with ethanolic alkali at an elevated temperature? (1+1+1+1)



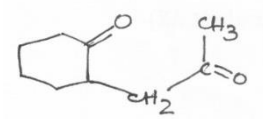
34. Mention two criteria for a good protecting group. Using protection/deprotection techniques, outline the following transformation. (1+2)



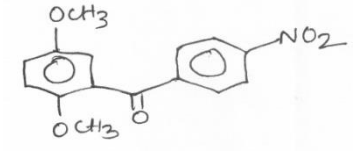
35. Identify A and B in the following sequence of reactions and suggest plausible mechanism for the transformation of A to B. (2)



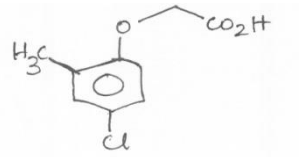
36. Write two different retrosynthesis and one synthesis of the following compound. (1+1+1+1)
    What happens when this compound is heated with aqueous ethanolic KOH?



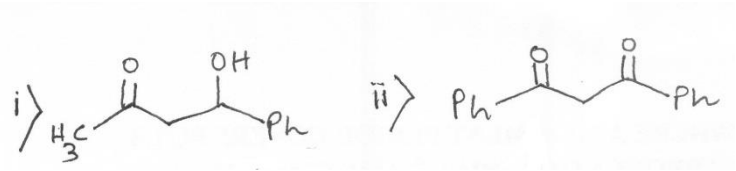
37. Alcoholic functionalities are often protected by making its t-butylether, as R-OH →R-OCMe$_3$.
    What advantage does this t-butyl group provide? Mention the protection and deprotection techniques also. (1+2)
38. Discuss possible retrosynthetic analysis and write one efficient synthesis of the following compound. (4)



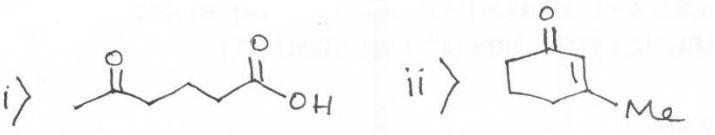
39. Write the synthesis of the following compound showing its retrosynthesis. (4)



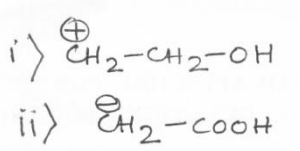
40. Give retrosynthetic analysis and efficient synthesis of the following compounds: (1+1+1.5+1.5)



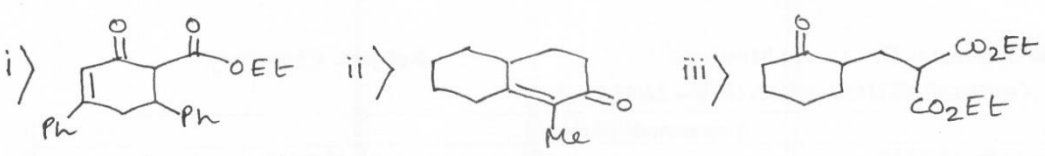
41. In protecting an aldehyde to a thioacetal, there is inversion of polarity at the carbonyl carbon, but no such effect is observed in case of oxyacetal of the aldehyde-explain. Write masking and unmasking procedures in both of the above cases. (2+1)
42. Give retrosynthetic analysis and efficient synthesis of the following. (3 each)



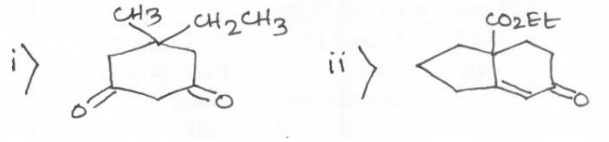
43. Give synthetic equivalents corresponding to the following synthons: (1 each)



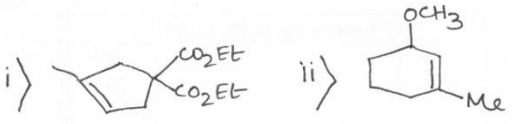
44. Give retrosynthetic analysis and an efficient synthesis of the following compounds. (2.5 each)



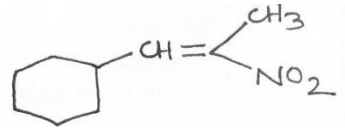
45. Depict the retrosynthesis and an efficient synthesis of the following compounds. (2.5 each)



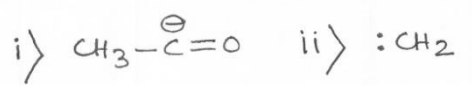
46. Give retrosynthetic analysis and an efficient synthesis of each of the following compounds. (2.5 each)



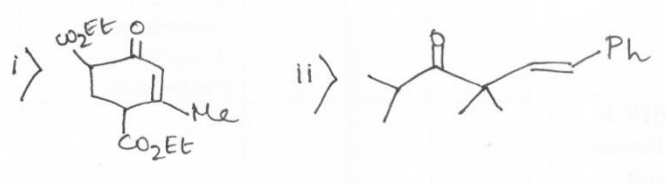
47. Starting from simple acyclic compounds, delineate how you would prepare the following compound. Show the retrosynthetic analysis in favour of your pursuance. (2.5)



48. What do you mean by nucleophilic and electrophilic synthons? Suggest one synthetic equivalent for each of the following: (1 each)



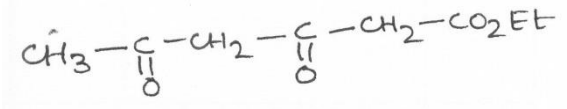
49. Give retrosynthetic analysis and synthesis of each of the following compounds. (3 each)



50. How would you convert: (1.5 each)

i) Cyclohexanone to 2,6-dimethylcyclohexanone

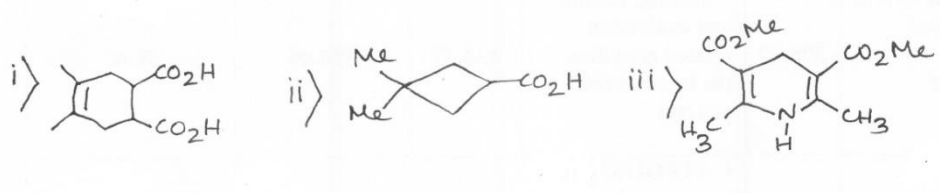
ii) Ethyl acetoacetate to



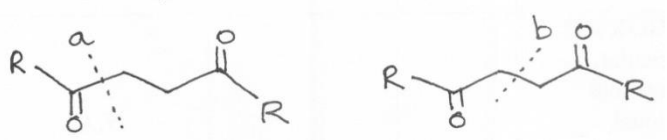
51. Carry out the conversion of ethylacetoacetate, using a suitable protecting group, to 3-oxabutan-1-ol. (2)

52. Show the patterns of latent polarities for 1,4-dioxygenated and 1,5-dioxygenated functions, and hence discuss their suitable disconnections in retrosynthetic analysis. (3)

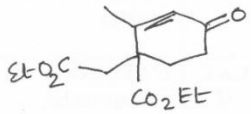
53. Give retrosynthetic analysis and efficient synthesis of each of the following compounds. (2.5 each)



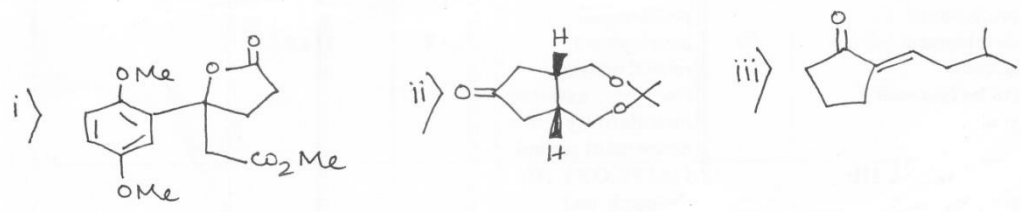
54. Two possible disconnections (a) and (b) of a target molecule are shown below. Obtain a pair of suitable synthons from each disconnection and indicate the umpolung synthon, is any. Give a synthetic equivalent for each synthon. (3)



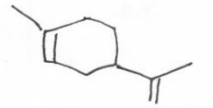
55. Give retrosynthetic route of the following compound and outline corresponding synthetic route. (2)



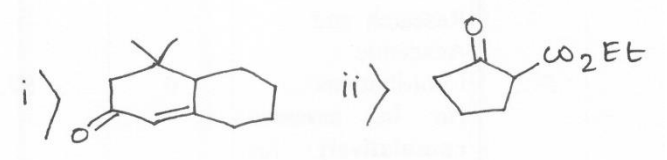
56. Give retrosynthetic route of the following compounds and outline corresponding synthetic routes (3)



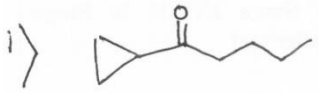
57. Using disconnection approach, propose suitable synthesis of: (2)

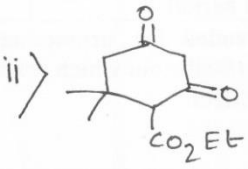


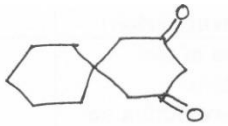
58. Give retrosynthetic analysis of the following compounds and outline corresponding synthetic route. (3)



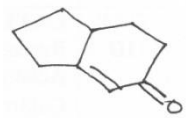
59. Highlighting retrosynthetic analysis, outline the synthetic route of the following compounds. (3 each)

i) 

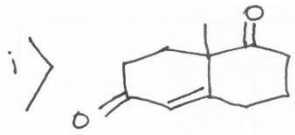
ii) 

iii) 

60. Depict the retrosynthetic analysis of the following compound and outline corresponding synthetic route. (3)

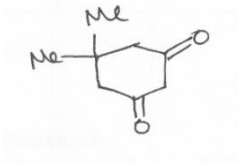


61. Indicating retrosynthetic analysis, give the synthetic route to the synthesis of the following compounds.

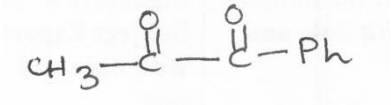
i) 

ii) 

62. How would you use a Michael reaction in one of the steps to prepare the following compound? Sketch the pathways with mechanism. (3)

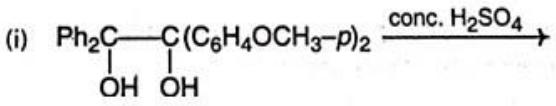


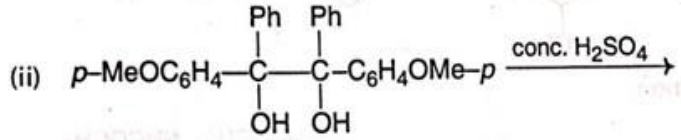
63. Show how you would synthesize the following compound using dithiane and other chemicals. (2)

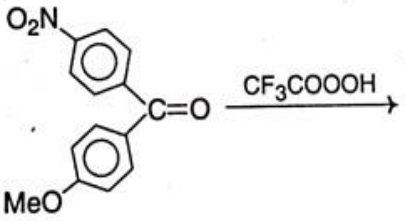


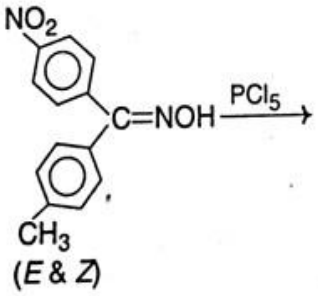
Rearrangements

1. Predict the product(s) with plausible mechanism in the following cases :

(i) 

(ii) 

(iii) 

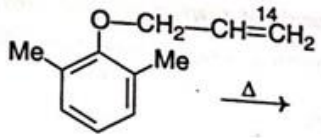
(iv) 

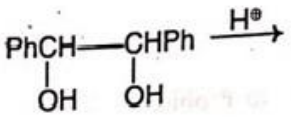
2. Give experimental evidence for the following :

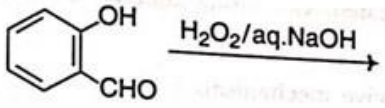
(i) Intramolecular nature of benzidine rearrangement.

(ii) Intermolecular nature of Fries rearrangement.

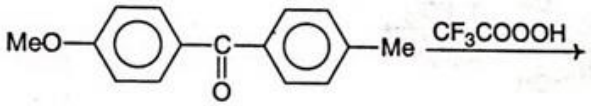
3. Predict the product(s) of the following reactions with plausible mechanistic interpretations :

(i) 

(ii) 

(iii) 

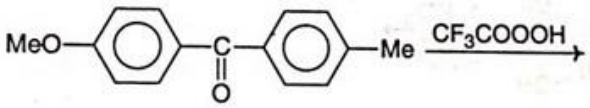
4. Predict the product formed in the following reaction with proper reaction mechanism :



5. Distinguish between the members of the following pairs by suitable chemical reaction :

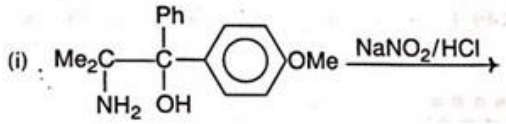
(*Z*)–benzaldoxime and (*E*)–benzaldoxime.

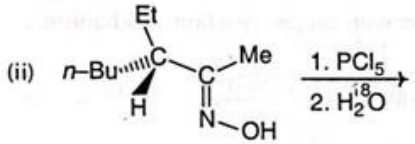
6. Predict the product formed in the following reaction with proper reaction mechanism :

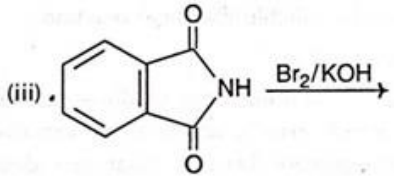


7. What happens when 9, 10–phenanthraquinone is heated with strong aqueous ethanolic KOH.

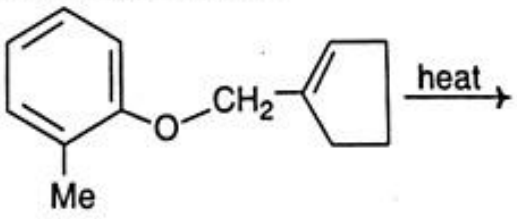
8. Predict the products of the following reactions and give mechanisms :

(i) 

(ii) 

(iii) 

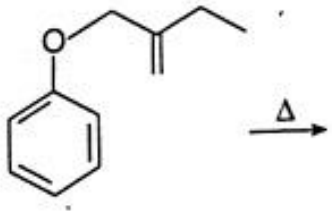
9. Predict the product of the following reaction :



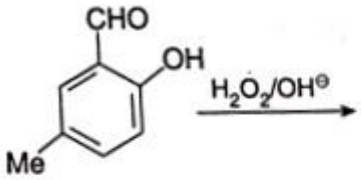
10. Predict the product of the following reaction with plausible mechanism :

$$CH_3CH(OH)C(OH)Ph_2 \xrightarrow{H^{\oplus}}$$

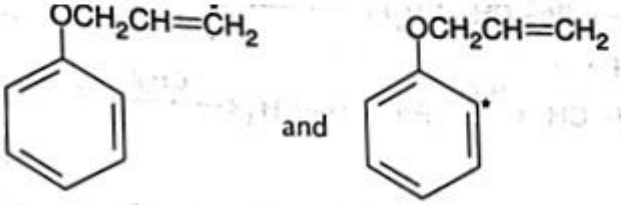
11. Identify the product of the following reaction with plausible mechanism :



12. Write the product of the following reaction and give plausible mechanism :

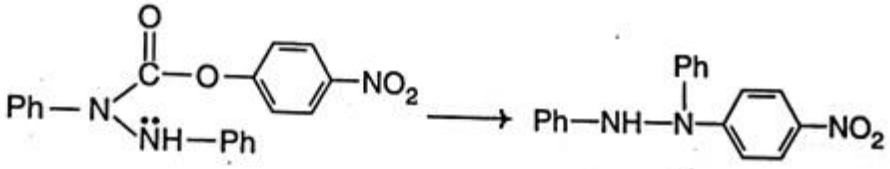


13. Write the structures of all possible products when a 1 : 1 mixture of

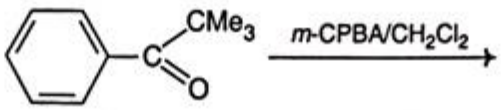


is heated together. Explain their formation. ($C^{*}=C^{14}$).

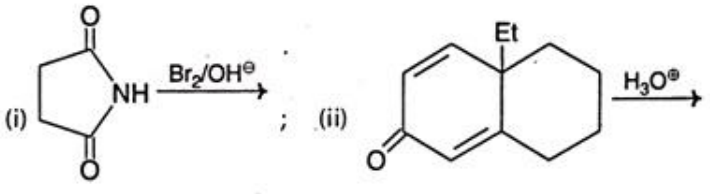
14. Suggest the reagent used in the following reaction and explain the reaction pathway.:

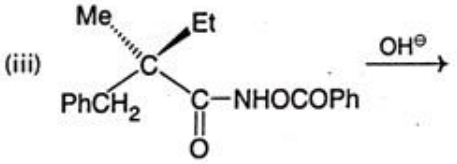


15. Predict the product of the following reaction and give mechanism :

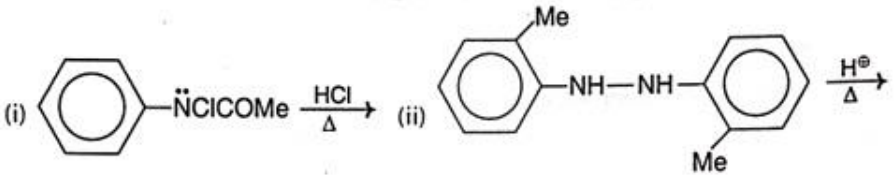


16. Predict the product of the following reactions and give plausible mechanisms :

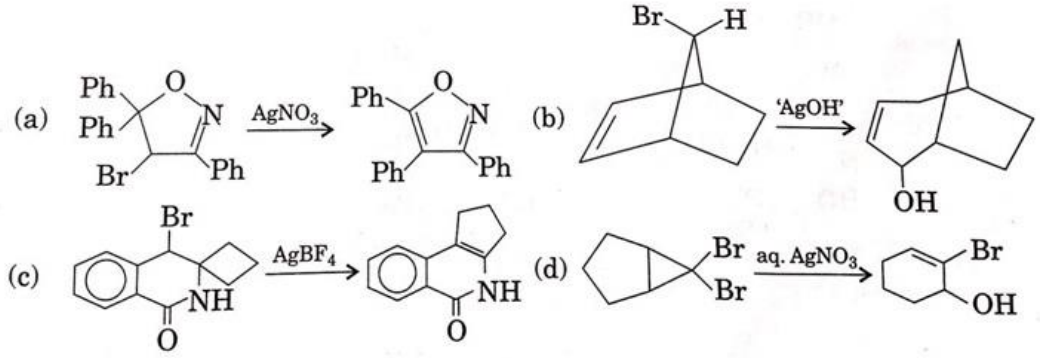




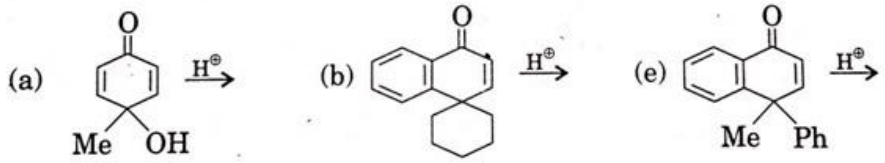
17. Predict the (major) product only and write mechanism to show their formation.



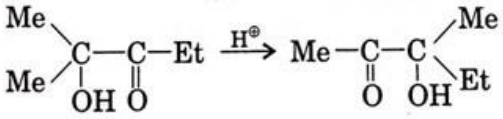
18. Suggest a mechanism for each of the following reactions:



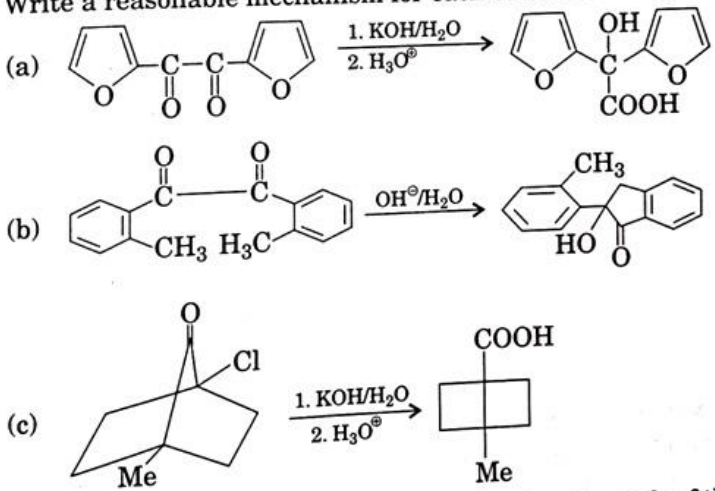
19. Predict the product and suggest a mechanism for each of the following dienone phenol rearrangements:



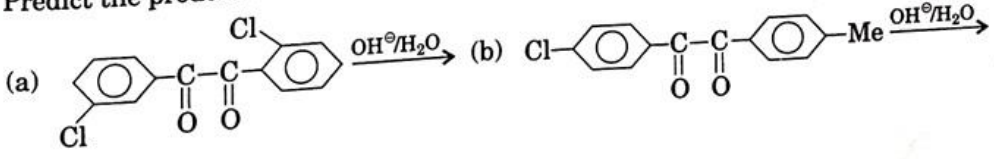
20. Rearrangement of α-hydroxyketone by the influence of acid is very similar dienone-phenol rearrangement. Propose a reasonable mechanism for the followi reaction:



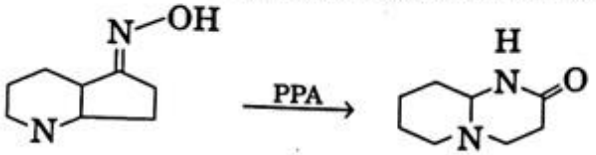
21. Write a reasonable mechanism for each of the following reactions:

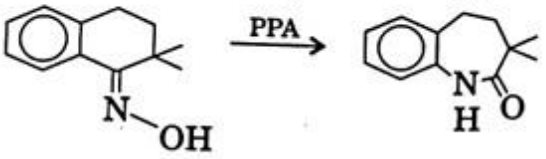


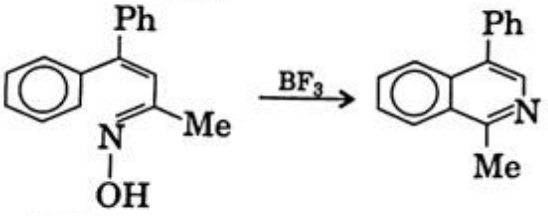
22. Predict the product and suggest a mechanism for each of the following reactions:

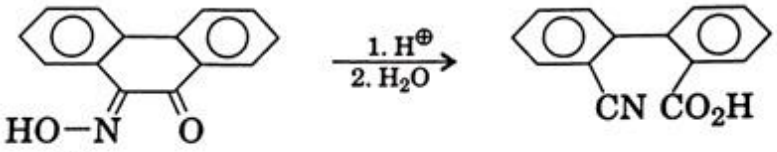


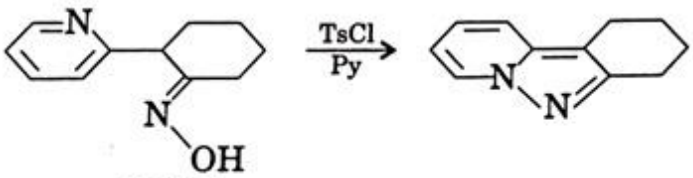
23. Write an arrow formalism mechanism for each of the following reactions:

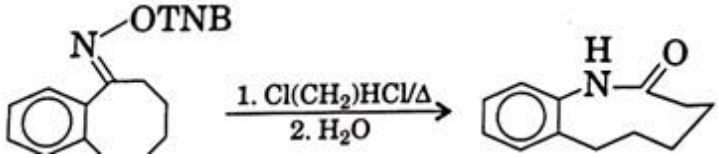
(a) 

(b) 

(c) 

(d) 

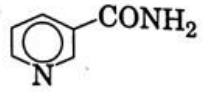
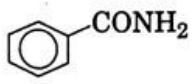
(e) 

(f) 

24. Which one of each of the following pairs will undergo the Hofmann rearrangement at a rate faster than the other and why?

(a) $PhCONH_2$ or p-$MeOC_6H_4CH_2CONH_2$

(b) $PhCH_2CONH_2$ or $PhCONH_2$

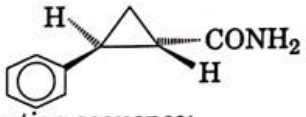
(c)  or 

25. A carboxylic acid can be converted to a primary amine (with one less carbon atom) by using the following reaction sequence:

$$R\text{–}COOH \xrightarrow[\text{or } PCl_5]{SOCl_2} R\text{–}COCl \xrightarrow{NH_3} RCONH_2 \xrightarrow{Br_2/NaOH} RNH_2$$

26. A primary amine obtained by this process is identified as (*S*)-3-methyl-3-hexanamine. Draw three-dimensional structures for all the four compounds involved in this reaction sequence and designate them as (*R*) or (*S*).

Predict the products formed when the following amides are treated with alkaline bromide water:

(a) $Ph(CH_2)_3CONH_2$ (b) $H_2NCO(CH_2)_4CONH_2$ (c) 

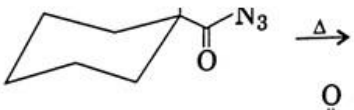
27. Identify the products A, B, C, D and E in the following reaction sequence:

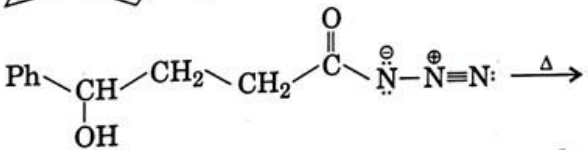
 $\xrightarrow{SOCl_2}$ A $\xrightarrow{NH_2NH_2}$ B $\xrightarrow{HNO_2}$ C $\xrightarrow[Me_3COH]{\Delta}$ D $\xrightarrow{CF_3COOH}$ E

28. Which one of the following azides will undergo the Curtius rearrangement at a faster rate and why?

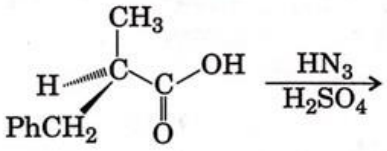
p-$MeOC_6H_4CON_3$ or $PhCON_3$

29. How can glycine be synthesized from diethyl malonate using the Curtius rearrangement?

(a) 

(b) 

30. Predict the product of the following reaction and give your reasoning:



31. Predict the products expected to be obtained when butanone is subjected to Schmidt rearrangement. Give mechanism and necessary explanation for the formation of these products.

32. Which one of the following two carboxylic acids will undergo the Schmidt rearrangement at a faster rate than the other and why?