PREVIOUS YEAR QUESTIONS (CU)

PERICYCLIC REACTIONS

CBCS, SEMESTER-5, CC-12

- 1. Why 2,3-ditertiarybutyl-1,3-diene does not undergo Diels-Alder reaction. (1M) [1a, CC-12, 2022]
- **2.** Why is conrotatory ring closure of $(4n + 2)\pi$ system photochemically allowed? (1M)

[1g, CC-12, 2022]

3. Predict the product of the following reaction and justify the formation in terms of FMO interaction. (3M)

4. Suggest mechanism for the following transformation and depict the stereochemistry of the chiral centre.? (2M)

5. Write the products when [A] is cyclised thermally and photochemically separately. Show FMO interaction and Woodward-Hofmann rule to explain the formation of products. (3M)

6. Why is the conrotatory ring closing of butadiene thermally allowed? (1M)

[1k, CC-12, 2021]

- 7. Depict the FMO interactions for $[\pi_s^4 + \pi_s^2]$ involving thermally allowed process. Explain why the reaction does not take place under photochemical conditions. (3M) [7a, CC-12, 2021]
- 8. Predict the product(s) with stereochemistry of the following reaction: (2M)

$$(E,E)$$
-CH₃CH=CHOCH₂CH=CHCH₃ $\stackrel{\triangle}{\longrightarrow}$ [7b, CC-12, 2021]

- 9. (2E,4E)-hexatriene is being separately cyclised by thermal and photochemical processes. Explain the formation of products showing FMO interaction. (3M)

 [11a, CC-12, 2022]
- **10.** Account for the fact that in cycloaddition reaction of cyclopentadiene with maleic anhydride the less stable *endo* adduct predominates. (2M)

 [11b, CC-12, 2021]
- 11. Write down the product of thermal sigmatropic reaction of the following molecule. (1M)

[1k, CC-12, 2020]

- **12.** Define pericyclic reaction. (1M) [1j, CC-12, 2020]
- 13. [2 + 2] Cycloaddition reaction is not a thermally favourable process. Why? (1M) [1k, CC-12, 2020]

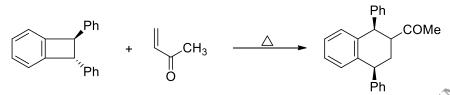
14. Predict the fate of the following compound **E** in the case of photochemical electrocyclic ring closure and explain the reaction on the basis of FMO theory: (3M)

15. Thermal [1,5]-H shift is facile but thermal [1,3]-H shift is not observed. Explain. (2M)

[6b, CC-12, 2020]

16. Rationalize the following reaction by FMO, showing the steps of the reaction: (3M)

7a, CC-12, 20201

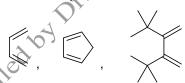


17. Using frontier orbital overlap, explain why Diels-Alder reaction between 1,3-butadiene and ethylene is thermally allowed but not catalysed by UV light. (2M)

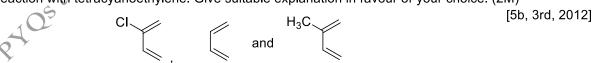
[7b, CC-12, 2020]

18. Arrange the following dienes in order of increasing reactivity in Diels-Alder cycloaddition reaction with tetracyanoethylene, with suitable explanation. (2M) [2b, 3rd, 2019]

- **19.** Cyclopentadiene undergoes thermal Diels-Alder reaction with maleic anhydride much faster than 1,3-butadiene. Explain this observation showing the adducts. (3M) [3a, 3rd, 2018]
- **20.** Arrange the following dienes in order of increasing reactivity in Diels-Alder cycloaddition with tetracyanoethylene. Give suitable explanation in favour of your choice. (2M) [2b, 3rd, 2017]



- **21.** Cyclopentadiene reacts with maleic anhydride much faster than 1,3-butadiene in a thermal Diels-Alder reaction. Explain this ovbservation showing the adducts. (3M) [5a, 3rd, 2015]
- **22.** Arrange the following dienes in order of increasing reactivity in Diels-Alder cycloaddition reaction with tetracyanoethylene. Give suitable explanation in favour of your choice. (2M)



23. Predict the products with stereochemistry (whereever applicable) in the following reactions and indicate the reaction pathways: (2M each) [9d, 5th, 2012]

24. Compare the rates of Diels Alder reaction of isoprene and 2-*t*-butyl-1,3-butadiene separately with tetracyanoethylene. (2M)

[10d, 5th, 2012]

25. Predict the product(s) of the following reactions with explanation. (2M each)

[10e, 5th, 2012]

(i) $Ph-C \equiv C-Ph$ + Me Me Me Me

(ii) Me Me Me

(iii) $\begin{array}{c} Ph \\ Ph \\ Ph \\ CD_3 \end{array} \longrightarrow$

(iv) OEt

OH

CH₃

CH₃

- **26.** Can you suggest a stereospecific method for converting *trans*-5,6-dimethyl-1,3-cyclohexadiene into *cis*-5,6-dimethyl-1,3-cyclohexadiene? (2M) [9e, 5th, 2011]
- 27. Predict the products of the following reactions and explain their formation: (1.5M each)

(i) Trans-2-butene $hv \rightarrow hv$ (ii) $\Delta \rightarrow D$ [9f, 5th, 2011]

28. Indicate the type of sigmatropic shifts with mechanism involved in the following transformation:

(2M each)

Me

Me

[9g, 5th, 2011]

Me

Me

Me

- **29.** Give the stereochemistry of the products formed when (i) *cis,trans*-2,4-hexadiene reacts thermally and (ii) *trans,trans*-2,4-hexadiene reacts photochemically and explain the reaction on the basis of FMO theory. (3M)

 [10c, 5th, 2011]
- **30.** Predict the product(s) and explain their formation for each of the following reaction: (2M each)

(i) H (ii) Cyclopentadiene warm [10d, 5th, 2011]

31. Predict the product(s) with stereochemistry of the following reaction: (2M) [9c(i), 5th, 2011]

(E,E)-CH₃CH=CHOCH₂CH=CHCH₃ \longrightarrow

32. Predict the product(s) with stereochemistry of the following reaction: (2M)

[9c(ii), 5th, 2011]

(Z)-2-butene $\frac{hv}{}$

- **33.** Depict the FMO interactions for $[^4\pi_s + ^2\pi_s]$ involving thermally allowed process. Explain why the reaction does not take place under prhotochemical conditions. (3M) [9d, 5th, 2011]
- 34. Thermal [1,5]-hydrogen shift is facile but [1,3]-hydrogen shift is not observed. (2M)

[10a(vi), 5th, 2011]

35. Compound (A) undergoes racemisation on heating. Explain. (2M)

[10a(vii), 5th, 2011]

36. Predict the product(s) with stereochemistry of the following reactions: (2M each)

[10b, 5th, 2011]

37. Predict the product of the following reaction. Give mechanism. (2M)

[9d, 5th, 2010]

38. Predict the product of the following reaction from FMO considerations: (2M)

[9e, 5th, 2010]

39. Write down the product of the following reaction which follows [3,3]-sigmatropic pathway and justify: (2M)

[9g, 5th, 2010]

- **40.** Using FMO approach, explain the product formed by the electrocyclic transformation of *trans*, *cis*, *trans*-2,4,6-octatriene under thermal condition. (3M) [10c, 5th, 2010]
- 41. Predict the major product of the following reaction. (1M)

[10d, 5th, 2010]

42. Cis-1,4-di-t-butylcyclohexane exists preferentially in the twist boat conformation. Explain. (1M)

[10e, 5th, 2010]

- **43.** Dewar benzene, a valence isomer of benzene, is much less stable than benzene. But once Dewar benzene is prepared, it can survide for a long time without ready conversion to benzene. Explain. (3M) [9d, 5th, 2010]
- 44. Explain the formation of the products. (2M each)

[9e, 5th, 2010]

(i) Octa-2E,4Z,6E-triene
$$\triangle$$
 CH_3

(ii) OMe OMe
$$OMe$$
 OMe OMe

45. Explain the following observation: (2M)

[10e, 5th, 2010]

46. Predict the product(s) with stereochemistry of the following reaction. Designate the pericyclic step involved. (2M) [10f, 5th, 2010]

47. Show the course of the following pericyclic reaction and explain the stereochemistry. (2M)

[10g, 5th, 2010]

48. Explain the following thermal reaction. (2M)

[9f, 5th, 2009]

49. Write the structures of I, J, and K as appear in the following sequence of reactions. (2M)

[9g, 5th, 2009]

$$\begin{array}{c|c} & & & \\ \hline & \\ \hline & & \\$$

50. Account for the following observation: (1.5M)

[10d, 5th, 2009]

$$CH_3$$
 CH_3

- **51.** Identify L in the following reaction and explain its formation. (2M)
- [10e, 5th, 2009]

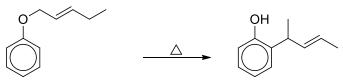
Me
$$CO_2C_2H_5$$
 $CO_2C_2H_5$ $CO_2C_2H_5$ $CO_2C_2H_5$

52. On thermal ring opening, *cis*-3,4-dimethylcyclobutene gives two dienes of which one is formed almost exclusively. Write the structure of this product and explain its formation. (3M)

[9d, 5th, 2009]

53. Give reasonable explanation of the following observation: (2M)

[9f, 5th, 2009]



54. Predict the products of the following reactions with plausible mechanism: (2M each)

OFt (10d, 5th, 2009)

- (ii) heat CH₃
- **55.** Using FMO approach, explain the product formed by the electrocyclic transformation of *trans,cis,trans*-2,4,6-octatriene. (2M) [10e, 5th, 2009]
- 56. Predict the products of the following reactions from FMO considerations. (2M each)

[9e, 5th, 2008]

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- (iii) hvo
- 57. Complete the following reactions from FMO considerations. (2M each)

[10f, 5th, 2008]

(i)
$$C_6H_5$$
 H C_6H_5

- 58. Justify the formation of the products of the following reaction from FMO considerations: (3M)

10g, 5th, 2008]

- 2 / \ _____
- **59.** Predict the product(s) of the following reactions with plausible mechanism. (2M)

[8c(iii), 5th, 2008]

- **60.** Using FMO approach, explain the product formed by the electrocyclic transformation of *trans,cis,trans*-2,4,6-octatriene under thermal condition. (3M) [9e, 5th, 2007]
- **61.** What products are obtained when each of the following compounds are separately heated? Also find out the absolute configuration of the chiral centres and *E/Z* configuration of the olefinic bond of the reactant and product in each case. (3M)

 [9f, 5th, 2007]

(i)
$$\underset{\text{Et}}{\underbrace{\hspace{1cm}}} \text{Me} \overset{\triangle}{\hspace{1cm}} \longrightarrow$$
 (ii) $\underset{\text{Me}}{\underbrace{\hspace{1cm}}} \text{H} \underset{\text{D}}{\hspace{1cm}} \longrightarrow$

62. Explain Claisen rearrangement as [3,3] sigmatropic reaction. (2M)

10e(i), 5th, 2007]

63. Write down the product of the following reaction which follows [3,3]-sigmatropic pathway and justify. (2M)

64. Predict the product of the following reaction from FMO considerations: (2M)

[10f, 5th, 2010]

- **65.** Using correlation diagram show that thermal dimerisation of ethylene is a disallowed interaction whereas photochemical dimerisation is an allowed process. (4M) [9e, 5th, 2006]
- **66.** What happens when *cis*-3,4-dimethyleyclobutene is heated with maleic anhydride? write the product with stereochemistry. (2M) [9f, 5th, 2006]
- **67.** Outline the synthesis of dewar benzene. Comment on its stability from symmetry point of view. (2M) [10e, 5th, 2006]
- **68.** Suggest mechanism for the following transformations and depict the absolute stereochemistry of the chiral centres in each case. (2M each)

 [10f, 5th, 2006]

(i)
$$heat$$
 $heat$ hea