# II.8 Pericyclic Reactions

Civil Services 2016–2026: **40** parts, **435** marks · IFoS 2016–2025: **36** parts, **235** marks

**Syllabus.** Classification and examples; Woodward-Hoffmann rules: electrocyclic reactions, cycloaddition reactions [2+2 and 4+2] and sigmatropic shifts [1, 3; 3, 3 and 1, 5], FMO approach.

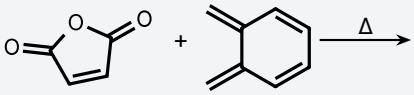
| Marks | 2016 | 2017 | 2018 | 2019 | 2020 | 2021 | 2022 | 2023 | 2024 | 2025 | 2026 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CSE | 25 | 60 | 35 | 25 | 65 | 30 | 35 | 50 | 25 | 45 | 40 |
| IFoS | 40 | 20 | 30 | 15 | 25 | 40 | 10 | 20 | 20 | 15 | |

**How to use this chapter.** Read every question once and mark the ones that repeat. Pick three, write them by hand against the clock (about 7 minutes for 10 marks), then compare with the model answers on vkcscience.com.

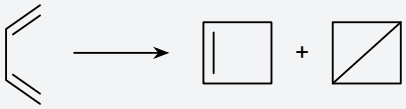
## 2026

### CSE 2026 · Q1(e) Diels–Alder of o-xylylene; photochemistry of butadiene [10 marks]

(i) Write the structures of two products formed in the following cycloaddition reaction, and mention the major and minor product with justification:



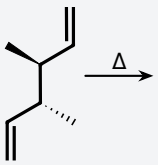

(ii) How may the following conversion be carried out? Draw the structures of transition state for both the products.




### CSE 2026 · Q4(a) Photo-electrocyclisation of hexa-2,4-diene; Cope rearrangement [15 marks]

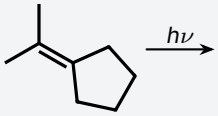
(i) Write the structure of the stereochemical product formed in the reaction of (2E,4E)-hexa-2,4-diene under photochemical conditions and explain using the FMO approach.

(ii) Identify the major product with correct stereochemistry in the following sigmatropic rearrangement:

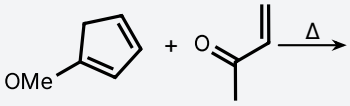



### CSE 2026 · Q4(b) Photochemical [1,3]-H shift; Diels–Alder of 1-methoxycyclopentadiene [15 marks]

(i) Write the product(s) of the following sigmatropic rearrangement and explain using the FMO approach:



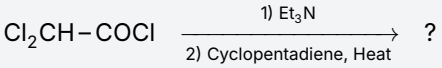

(ii) Write the major product showing correct stereochemistry of the following cycloaddition reaction:



# 2025

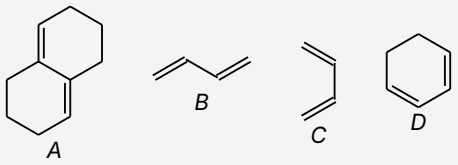
## CSE 2025 · Q5(a) Dichloroacetyl chloride with $Et_3N$, then cyclopentadiene [10 marks]

Write the structure of the product(s) and the intermediate formed in the following reaction:

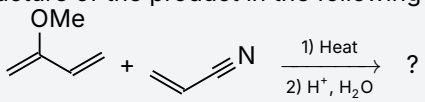



## CSE 2025 · Q7(b) Diels–Alder reactivity of four dienes; 2-Methoxybutadiene with acrylonitrile [15 marks]

(i) Rank the following dienes in order of increasing reactivity in a Diels-Alder reaction (1 = least reactive, 4 = most reactive). Briefly explain your answer: 10

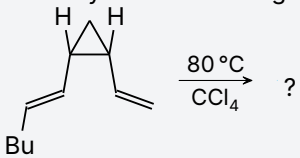



(ii) Write the structure of the product in the following reaction: 5

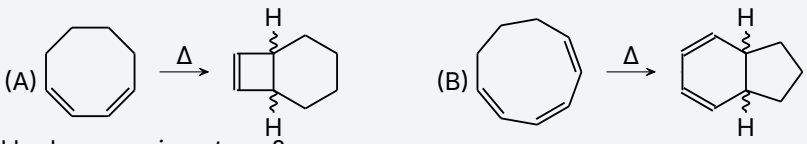



## CSE 2025 · Q7(c) Rearrangement of a cis-divinylcyclopropane; Mode of ring closure in two electrocyclic reactions [20 marks]

(i) Write the structure of the product formed in the following sigmatropic rearrangement and categorize it with suitable explanation. Explain the thermal feasibility of this rearrangement by drawing orbital diagram: 10



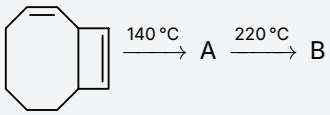

(ii) (1) Identify the mode of ring closure for each of the following electrocyclic reactions: 10




(2) Are the indicated hydrogens *cis* or *trans*?

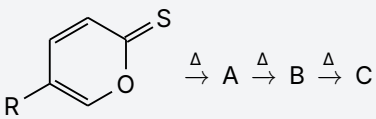
## IFoS 2025 · Q1(g) Two thermal electrocyclic steps [5 marks]

Indicate the products in the following sequence of reactions :




## IFoS 2025 · Q2(d) Thermal oxygen–sulfur interchange [10 marks]

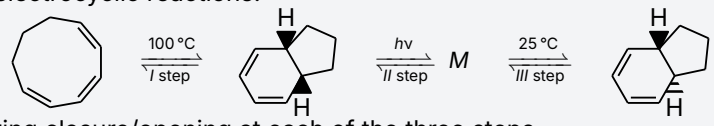
Write the products A, B and C in the following transformation indicating the processes involved and electron flow :



# 2024

## CSE 2024 · Q1(e) Electrocyclic steps of cyclononatriene [10 marks]

Consider the following electrocyclic reactions:



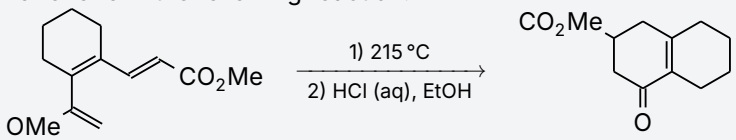

(i) Predict the mode of ring closure/opening at each of the three steps.

(ii) Predict the structure of *M*.

(iii) Are the indicated hydrogens *cis* or *trans*?

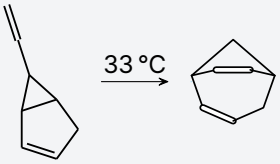
## CSE 2024 · Q3(b) Enone from a methoxy triene; Classify the rearrangement at 33 °C; Methoxy methyl benzoquinone with butadiene [15 marks]

(i) Explain the formation of enone in the following reaction:



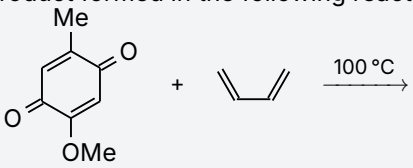

5

(ii) Classify the following sigmatropic rearrangement and comment if it is symmetry-allowed or symmetry-forbidden:




5

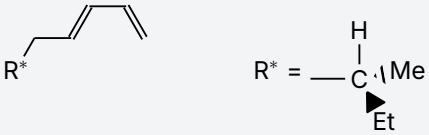
(iii) Write the structure of the major product formed in the following reaction:




5

## IFoS 2024 · Q1(g) Photochemical alkyl migration [5 marks]

How does migration of R* group involving photochemical [1, 5] sigmatropic rearrangement in the following compound proceed with inversion of configuration? Explain :



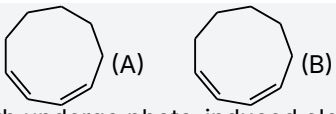

## IFoS 2024 · Q3(c) Endo selectivity in a Diels–Alder reaction; Electrocyclic closure of an E,Z diene [15 marks]

(i) In the cycloaddition reaction of cyclopentadiene with maleic anhydride, the endo product is preferred even though the endo product is less stable than the exo product. Explain. 10

(ii) Write the product indicating stereochemistry when 2*E*, 4*Z*-hexadiene is undergoing thermal as well as photochemical reaction. 5

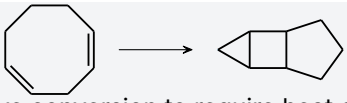
# 2023

### CSE 2023 · Q1(d) Photochemical electrocyclic closure of two cyclonona-1,3-dienes [10 marks]




The above compounds both undergo photo-induced electrocyclic reactions. What are the structures and stereochemistry of the products?

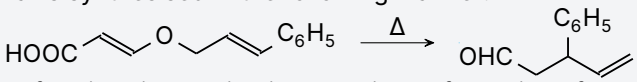
### CSE 2023 · Q3(a) Cycloocta-1,4-diene to a tricyclic isomer: heat or light [15 marks]



Would you expect the above conversion to require heat or light? Explain using molecular orbital diagram.

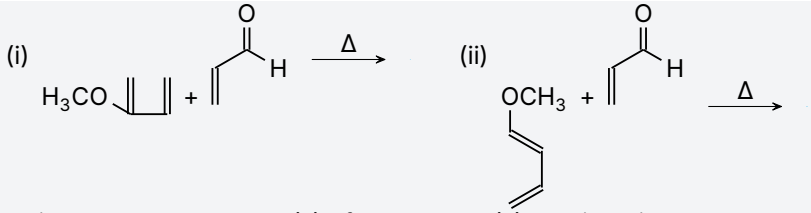
### CSE 2023 · Q3(b) 3-Phenyl-4-pentenal from 3-(cinnamyloxy)acrylic acid [15 marks]

3-Phenyl-4-pentenal is synthesised in the following manner:




(i) Identify the type of pericyclic reaction involved in the formation of unsaturated intermediate.
(ii) What elements are lost when the intermediate is converted to 3-phenyl-4-pentenal?
(iii) Identify the carbon atom in the starting acrylic acid that becomes the aldehyde carbon in the pentenal.
(iv) Write the steps involved for this transformation.

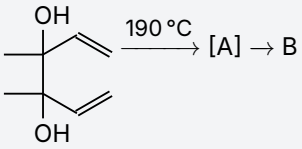
### CSE 2023 · Q3(d) Methoxybutadienes with acrolein [10 marks]




Write down the structure(s) of the product(s) obtained in the above reactions. Provide suitable justification and propose the mechanisms.

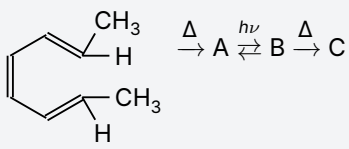
### IFoS 2023 · Q1(g) A double oxy-Cope rearrangement [5 marks]

Identify A and B in the following reaction :



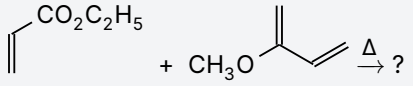

### IFoS 2023 · Q3(f) Six-pi electrocyclic switching [10 marks]

Complete the following reaction sequence by writing the structures of A, B and C. Also write the name of the process involved.



### IFoS 2023 · Q4(c) Regioselective Diels–Alder addition [5 marks]

Indicating the product spread, complete the following pericyclic reaction :



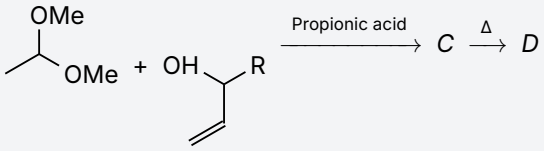

## 2022

### CSE 2022 · Q1(e) Heating cyclopentadiene [10 marks]

Predict the product(s) formed on heating the cyclopentadiene and provide a suitable justification to your answer.

### CSE 2022 · Q3(a) Acetal and ortho-ester Claisen rearrangements of an allylic alcohol [15 marks]

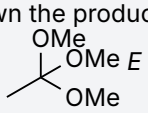
The compound *A*, acetal of acetaldehyde, on reaction with *B*, under given reaction conditions, yields *C* and the final product *D*:




*A* *B*

(i) Write down the structures of the products *C* and *D*. Propose a mechanism with suitable explanation.

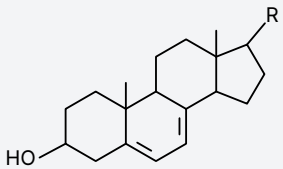
(ii) Write down the product(s) if *ortho*-ester *E* is used instead of the compound *A* under the similar reaction conditions:



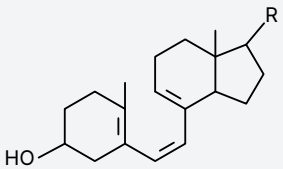

*E*

### CSE 2022 · Q3(b)(i) Ergosterol, precalciferol and the need for sunlight [10 marks]

(i) Considering the structural features of ergosterol (*A*) and precalciferol (*B*), a precursor of vitamin D, giving mechanistic details, explain why vitamin D deficiency is endemic in those parts of the world where sunlight is scarce.




*A*




*B*

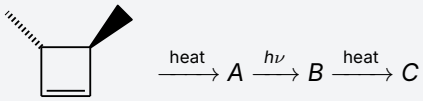
10

### IFoS 2022 · Q3(b) Steric control of Diels–Alder reactivity [5 marks]

Explain the reactive behaviour of 2,3-di-*t*-butylbuta-1,3-diene (*A*) and 1,3-di-*t*-butylbuta-1,3-diene (*B*) as dienes for Diels–Alder reaction.

### IFoS 2022 · Q4(e) Thermal–photochemical–thermal switching [5 marks]

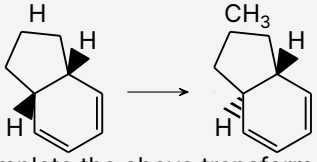
Identify *A*, *B* and *C* in the following chemical sequence:



# 2021

### CSE 2021 · Q1(e) Two transformations by electrocyclic relays [10 marks]

(i) 

(ii) 

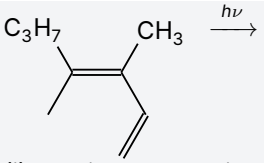
Complete the above transformations.

### CSE 2021 · Q4(a) Deuterium scrambling on heating 3-deuteroindene; Cyclopentadiene with maleic anhydride [20 marks]

(i) Heating of 3-deuteroindene causes scrambling of the deuterium. Explain with mechanism.

(ii) Write the structure of product(s) formed during the thermal reaction of maleic anhydride with cyclopentadiene. Explain with mechanism.

### IFoS 2021 · Q1(b) Photochemical hydrogen migration in a diene [5 marks]



(i) Predict the reaction mechanism and configuration of the excited state of the above reaction.

(ii) Using FMO approach, explain the reason for migration of hydrogen.

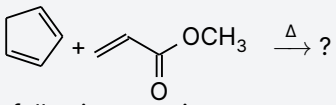
### IFoS 2021 · Q2(a) Thermal closure of octatriene [10 marks]

2,4,6-octatriene – [E, E] $\xrightarrow[\text{disrotatory}]{\Delta}$ ?

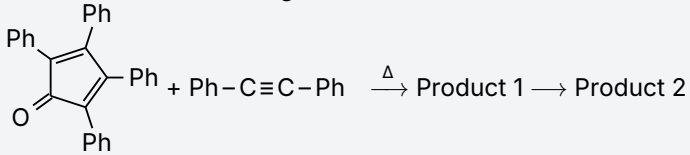
Using FMO approach, draw Pi molecular orbitals showing mirror plane symmetry and suggest reaction mechanism and product with stereochemistry.

### IFoS 2021 · Q4(a) Cyclopentadiene and methyl acrylate; Tetraphenylcyclopentadienone cycloaddition [10 marks]

(i) Write the product of the following reaction and justify the stereospecificity of the reaction with the help of formation of proper transition state: 5



(ii) Identify the products 1 and 2 from the following reaction: 5



### IFoS 2021 · Q7(b) Ireland–Claisen rearrangement of an allylic acetate [10 marks]

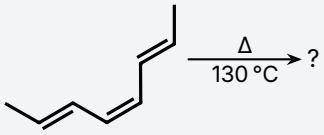
Write the product of the following reaction and give suitable mechanism:

*cis*-cyclohex-3-ene-1,2-diyl diacetate (drawn: both OAc wedged) $\xrightarrow[\text{TBDMSCl}]{\text{LDA, } -78\,^\circ\text{C}}$ ?

## 2020

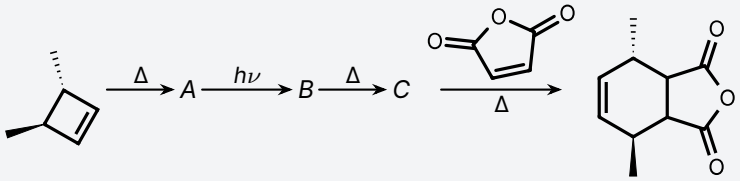
### CSE 2020 · Q1(e) Thermal electrocyclisation of (2E,4Z,6E)-octa-2,4,6-triene [10 marks]

Predict the major product, and identify the type and stereochemical mode of the following reaction:




### CSE 2020 · Q2(a) Cyclobutene ring opening and closing, then Diels–Alder [15 marks]

Complete the following conversion writing missing intermediate compounds *A*, *B* and *C*:




### CSE 2020 · Q2(b) Hückel–Möbius (PMO) analysis of cycloadditions [15 marks]

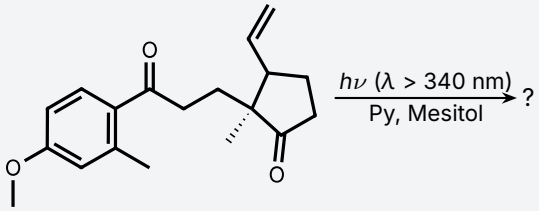
Match Column—I (Cycloadditions) with Column—II (Hückel-Möbius systems) using PMO approach:

| *Column—I* | *Column—II* |
|---|---|
| *I* : [2s+2s] | *A* = An, M, *hν*-allowed |
| *II* : [4s+2a] | *B* = A, H, Δ-allowed |
| *III* : [4s+2s] | *C* = A, M, Δ-allowed |
| *IV* : [2a+2s] | *D* = An, H, *hν*-allowed |

where An = Antiaromatic, A = Aromatic, M = Möbius, H = Hückel, Δ = Thermally, *hν* = Photochemically.

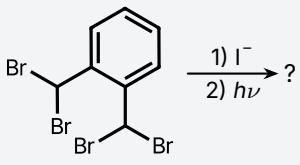
### CSE 2020 · Q5(c) Photoenolisation and intramolecular Diels–Alder: estrone skeleton [10 marks]

Complete the following reaction giving the structures of intermediates involved:




### CSE 2020 · Q6(b) o-Xylylene from a tetrabromide; photochemical ring closure [15 marks]

Complete the conversion given below writing intermediate steps involved:

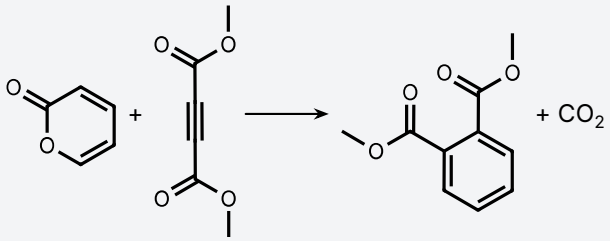


### IFoS 2020 · Q1(a) Crossover experiment: the Claisen rearrangement is intramolecular [5 marks]

With a suitable cross-over experiment, prove that the Claisen rearrangement proceeds intramolecularly.

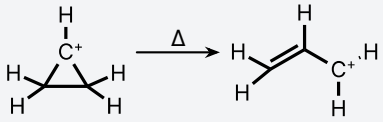
### IFoS 2020 · Q1(g) 2-Pyrone + DMAD: Diels–Alder then retro-Diels–Alder losing $CO_2$ [5 marks]

The following reaction is known to occur in two thermally allowed steps. Show the structure of the intermediate in the reaction and explain why each step is allowed.




### IFoS 2020 · Q3(b) Cyclopropyl to allyl cation: electrocyclic ring opening and stereochemistry [10 marks]

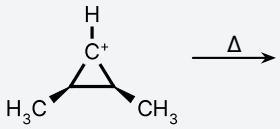
Cyclopropyl carbocations react rapidly to form allyl carbocations.




What kind of pericyclic reaction is this?

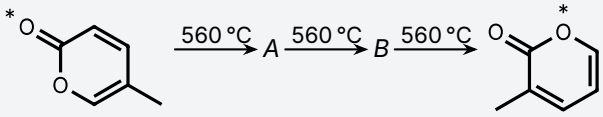
Explain why the allyl carbocation is more stable than the cyclopropyl carbocation.

Predict the stereochemistry of the allyl carbocation that is formed from the following *cis*-dimethylcyclopropyl carbocation:




### IFoS 2020 · Q4(b) $^{18}$O-labelled 2-pyranone scrambling at 560°C [5 marks]

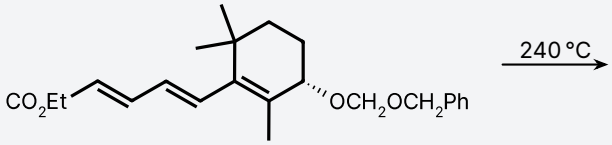
Explain the following transformation by identifying the intermediates *A* and *B*. Also identify the types of pericyclic reactions involved along with their stereochemical modes.




## 2019

### CSE 2019 · Q1(e) Thermal 6π electrocyclisation of a dienyl cyclohexene [10 marks]

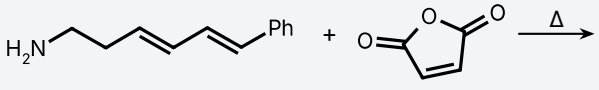
Write the product of the following reaction and comment on the stereochemistry of the product:

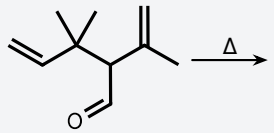
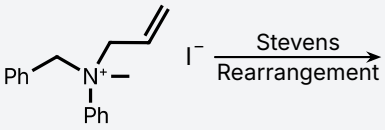



### CSE 2019 · Q2(a) Diels–Alder and lactam closure; Cope; Stevens [15 marks]

Predict the structure of the products in the following reactions:

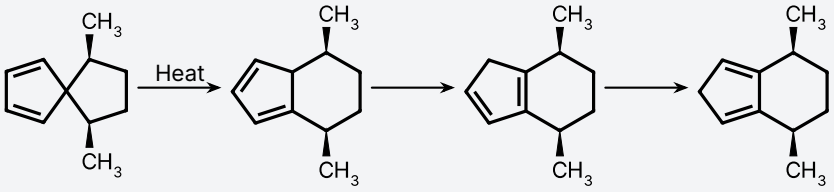
(i)



(ii)  (iii) 

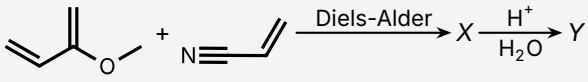
### IFoS 2019 · Q1(e) Sigmatropic shifts in a spiro-diene rearrangement [5 marks]

Indicate what types of sigmatropic reactions are involved in the following transformations:



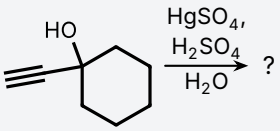
### IFoS 2019 · Q3(d) Regioselective Diels–Alder of 2-methoxybutadiene with acrylonitrile; hydration of an ethynyl carbinol [10 marks]

(i) In the following reaction, there is a possibility of formation of two isomeric products *Y*. However, one isomer is formed. Identify both the isomers *Y* and also the structure of the most likely formed product:



5

(ii) Identify the product:



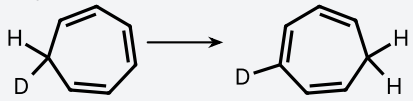
5

## 2018

### CSE 2018 · Q1(d) Thermal [1,3]- and [1,5]-hydrogen shifts [10 marks]

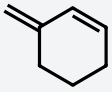
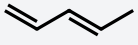
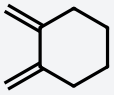
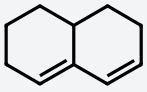
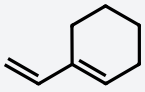
Which of the following known sigmatropic rearrangements would proceed readily and which slowly? Explain your answers :

(i) $CH_3-CH=CD_2 \longrightarrow CH_2=CH-CHD_2$

(ii) 

### CSE 2018 · Q4(a) Which dienes cannot take part in a Diels–Alder reaction [10 marks]

Which of the following conjugated dienes would not react with a dienophile in Diels-Alder reaction? Justify your answer :

(i)  (ii)  (iii)  (iv)  (v) 

### CSE 2018 · Q4(c) Maleic anhydride: fast [4+2] with butadiene, no thermal [2+2] with ethene [15 marks]

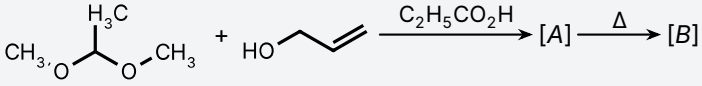
Maleic anhydride reacts rapidly with 1,3-butadiene, but does not react at all with ethene under thermal conditions. Explain.

### IFoS 2018 · Q1(f) 2-Methylcyclohexadiene with DMAD: Diels–Alder then retro-Diels–Alder [5 marks]

The initial product formed from the reaction of 2-methylcyclohexadiene and dimethylacetylene dicarboxylate on heating is transformed to another product with elimination of a small molecule. Write the structure of each product (initial and final). Also write how these are formed.

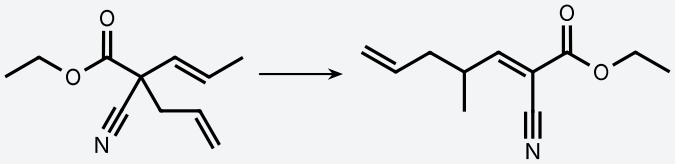
### IFoS 2018 · Q2(c) Johnson orthoester Claisen rearrangement [10 marks]

Write the structures of [*A*] and [*B*] of the following sequence of reactions. Write the mechanism of their formation. What type of rearrangement and electronic shift are involved in the second step?



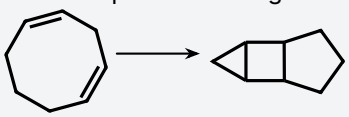

### IFoS 2018 · Q3(f) Classifying a sigmatropic shift of a cyano ester [5 marks]

Classify the following sigmatropic rearrangement and suggest if it would proceed readily or slowly. Explain your answer:



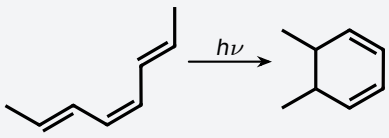

### IFoS 2018 · Q4(f) Cyclooctatriene to a bicyclic: heat or light? [5 marks]

Would you require the following conversion to require heat or light? Explain.



### IFoS 2018 · Q5(h) Photochemical ring closure of a dimethylhexatriene: stereochemistry [5 marks]

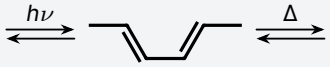
Predict the stereochemistry of the product in the following reaction:




## 2017

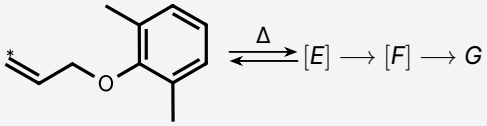
### CSE 2017 · Q1(e) Electrocyclic closure of (2E,4E)-hexa-2,4-diene: FMO [10 marks]

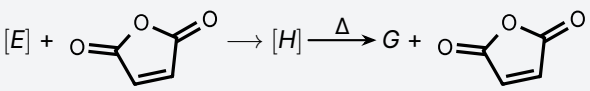
Write the structure of the product with proper stereochemical outcome, in each of the following reactions and justify your answers with the help of FMO theory.




### CSE 2017 · Q2(a) Labelled allyl aryl ether: Claisen, Cope and a Diels–Alder trap [10 marks]

Give the structures of *E* to *H* showing the position of the labelled carbon [∗] in each.



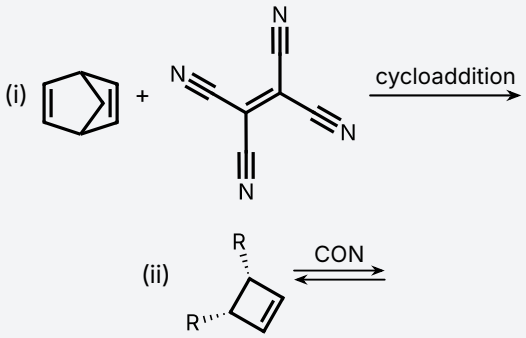



### CSE 2017 · Q5(a) Thermally forbidden [1,3]-H shift; rules for sigmatropic reactions [10 marks]

Explain why concerted 1,3-sigmatropic shift of hydrogen is thermally forbidden and give Woodward-Hoffmann selection rules for sigmatropic rearrangement reactions.

### CSE 2017 · Q6(a) Norbornadiene with TCNE; ring opening of a cis-cyclobutene [10 marks]

Predict the products of the following reactions.

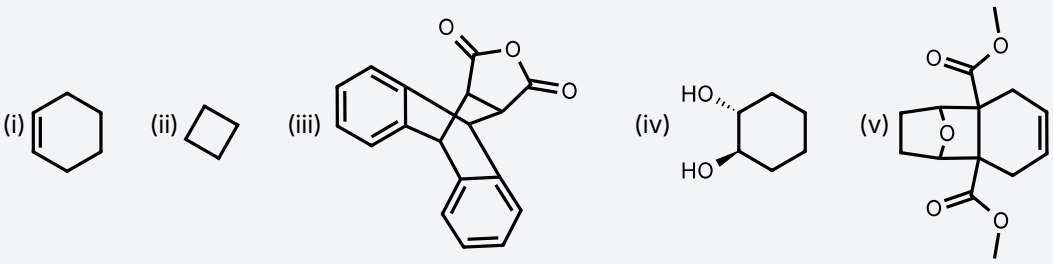



### CSE 2017 · Q6(b) Thermal cyclisation of pentadienyl anion and cation [10 marks]

What will be the stereochemical course of thermal cyclization of (i) Pentadienyl anion, and (ii) Pentadienyl cation?

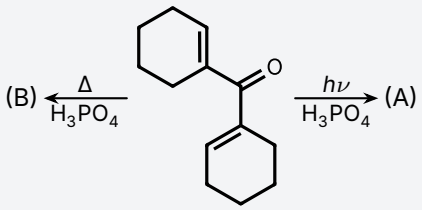
### CSE 2017 · Q8(e) Preparation of five compounds (pericyclic routes) [10 marks]

How do you prepare the following compounds?



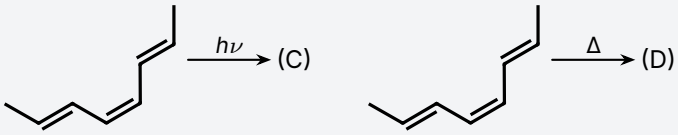

### IFoS 2017 · Q7(a) Thermal and photochemical ring closure of a hexatriene [10 marks]

(i) Give stereochemisty of the product of the given reaction:




5

(ii) Complete the following reaction:




5

**IFoS 2017 · Q7(d) Ethene + allyl cation by Woodward–Hoffmann rules** [10 marks]

Predict the reaction between ethene and allyl cation in the light of Woodward-Hoffmann rules.

## 2016

**CSE 2016 · Q5(a) [1,5]-Hydrogen shift in penta-1,3-diene: FMO treatment** [10 marks]

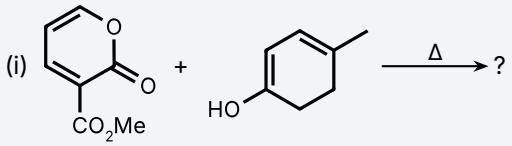
Give the Woodward-Hoffmann rule for sigmatropic rearrangement for 1,5-shift involving hydrogen in pentadiene. Illustrate with FMO approach.

**CSE 2016 · Q7(b) Electrocyclic reactions: hexatriene, pentadiene, and ethene** [15 marks]

Write the product for the electrocyclic reaction of the following:
(i) $CH_2=CH-CH=CH-CH=CH_2$
(ii) $CH_3-CH_2-CH=C=CH_2$
(iii) 2 $CH_2=CH_2$

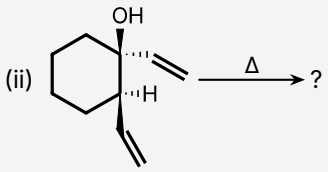
**IFoS 2016 · Q3(b)(i) 2-Pyrone + dienol: inverse-demand Diels–Alder, loss of $CO_2$ and water** [5 marks]

Complete the following pericyclic reactions:




**IFoS 2016 · Q3(b)(ii) trans-1,2-Divinylcyclohexanol: oxy-Cope ring expansion** [5 marks]

Complete the following pericyclic reactions:

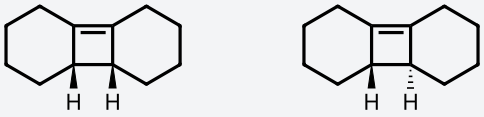



**IFoS 2016 · Q3(c)(i) Correlation diagrams: butadiene and cyclobutene** [5 marks]

Explain correlation diagrams for electrocyclic interconversion of 1,3-butadiene and cyclobutene.

### IFoS 2016 · Q3(c)(ii) Fused cyclobutenes: conrotatory opening allowed or blocked [5 marks]

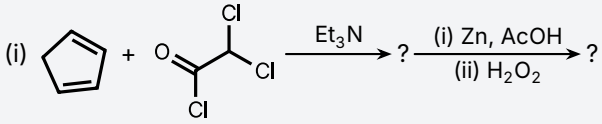
One of the cyclobutenes on heating reacts very fast while the other reacts at extremely slow rate. Explain.




A B

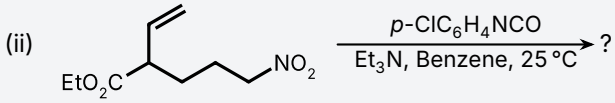
### IFoS 2016 · Q3(d)(i) Dichloroketene [2+2], dechlorination, Baeyer–Villiger [5 marks]

Write the products in the following reactions:




### IFoS 2016 · Q3(d)(ii) Nitrile oxide from a nitro compound: intramolecular [3+2] [5 marks]

Write the products in the following reactions:




### IFoS 2016 · Q8(a)(i) Cyclopentadiene + β-nitrostyrene; Nef reaction of the adduct [10 marks]

Complete the reactions and give appropriate mechanisms of the following :

