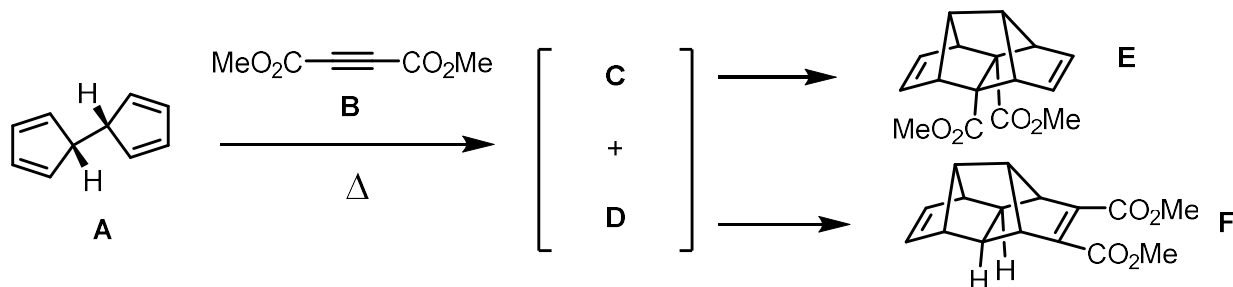


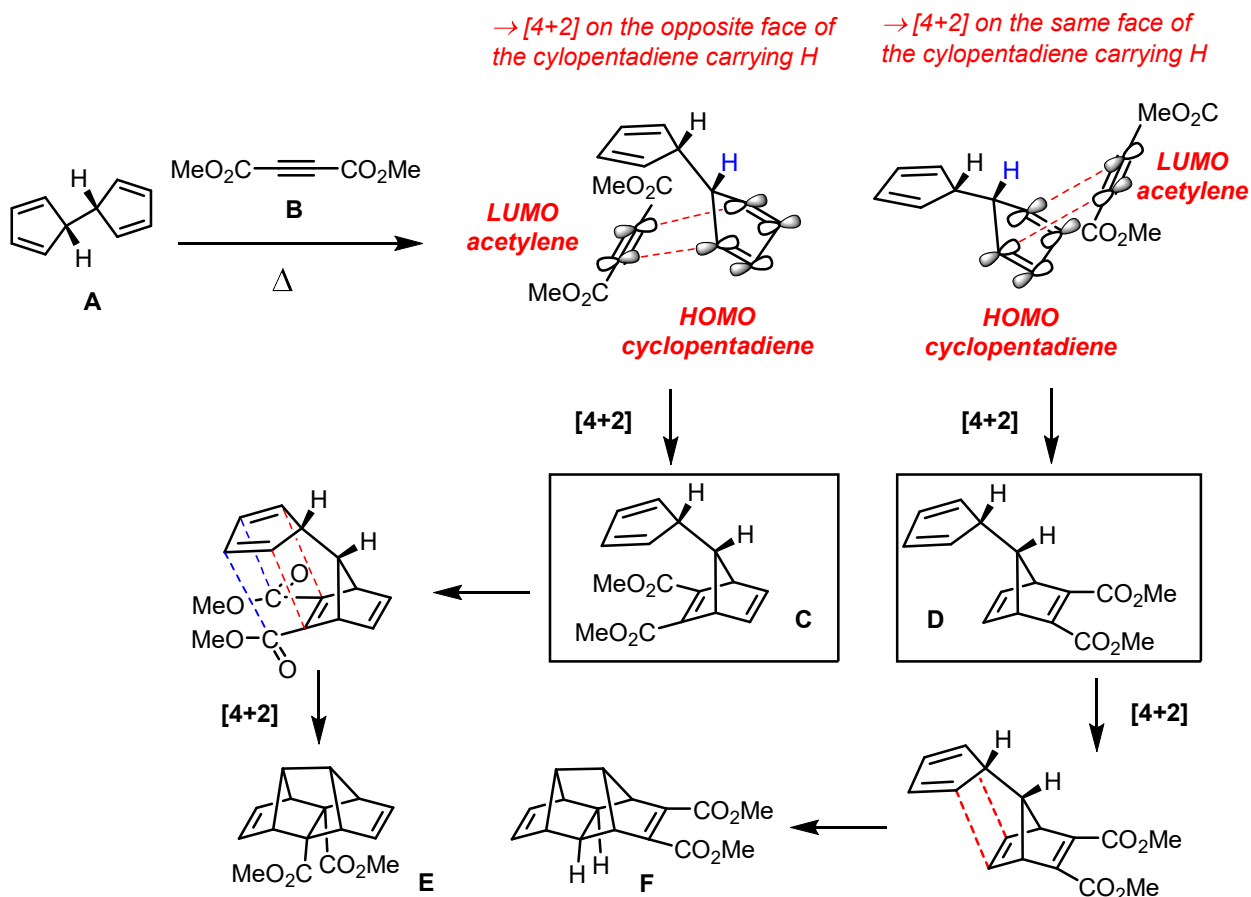
Question	Subject	# Pts
1	Pericyclic Reactions	≈ 14
2	Pericyclic Reactions	≈ 6
3	Pericyclic Reactions	≈ 8
4	Pericyclic Reactions	≈ 18
BONUS	Pericyclic Reactions	4



When the bis-cyclopentadiene **A** is combined with the dimethylacetylene dicarboxylate **B** and the mixture is heated, products **C** and **D** are formed each of which has four unsaturations. These compounds undergo subsequent reactions to give **E** and **F** as the final products.

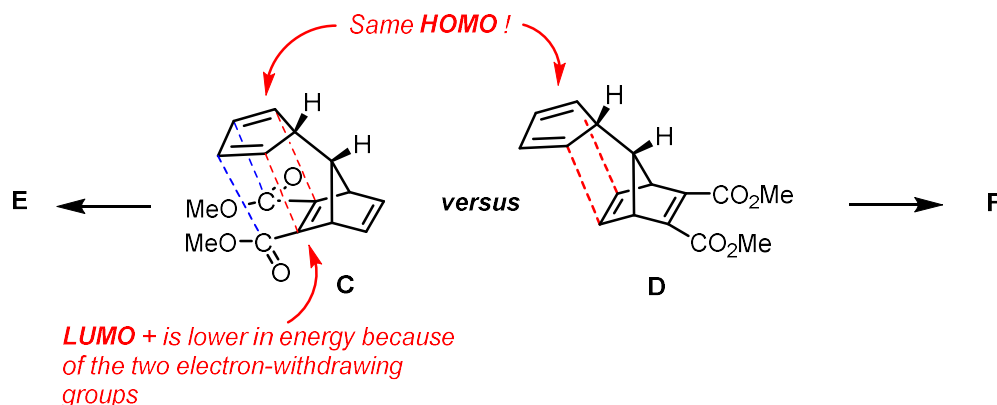
- a) Propose structures for intermediates **C** and **D** and explain their formation using frontier molecular orbital (FMO) theory.

(2pts struc. **C**, 2 pts. Struct. **D**, 2pts HOMO, 2pts LUMO)

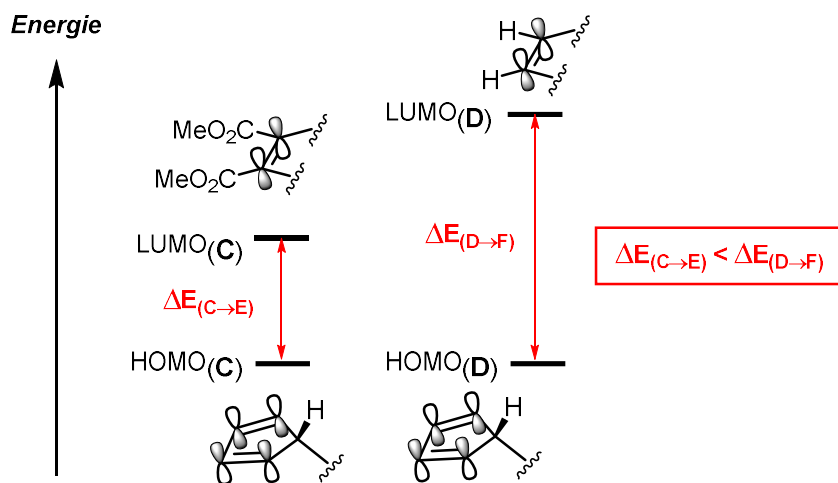


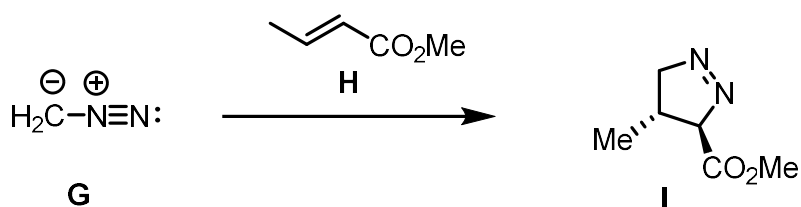
b). Which transformations do you think will be more rapid – that which yields **E** from **C** or that which yields **F** from **D**? Explain your choice with the aid of a potential energy diagram wherein the barrier heights for the two reactions reflect the energy differences in the interacting FMOs.

(2 pts faster, 2 pts LUMO with EWG esters, 2 pts diagram)



The HOMO has the same energy in both transformations. The LUMO is lower in energy for transformation C to E. As a result the difference in energy between the HOMO and LUMO will be smaller facilitating a faster reaction (lower barrier). A potential energy diagram follows :

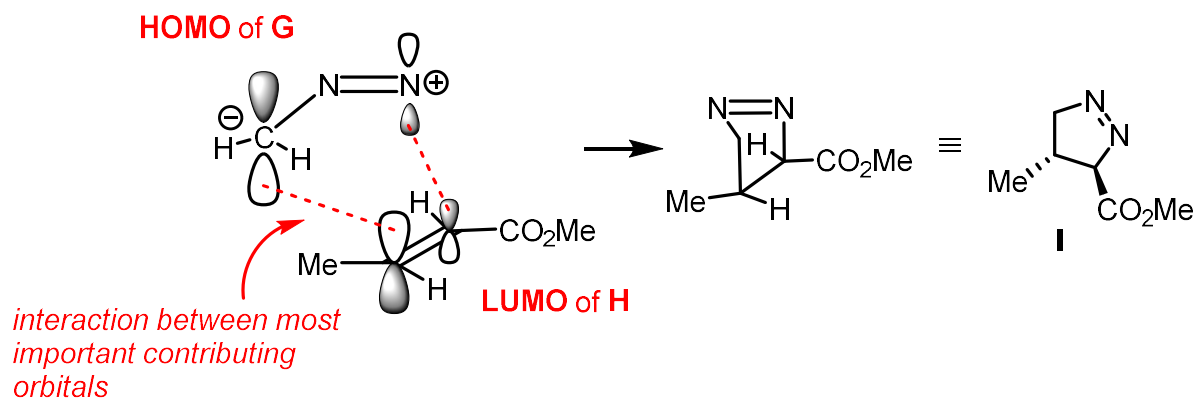


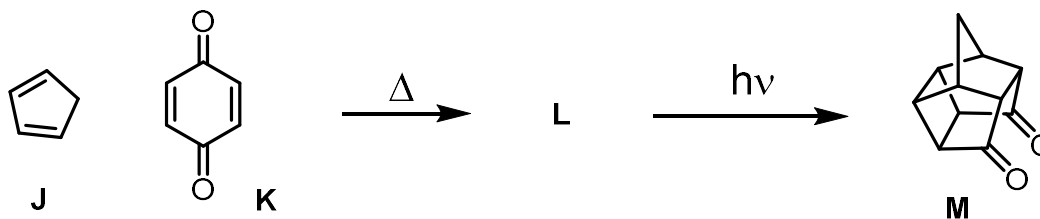


Diazomethane (**G**) reacts with the α,β -unsaturated ester **H** to **I**. Using FMO theory, justify the regio and stereochemical outcome of the reaction.

(2 pts HOMO, 2 pts LUMO, 2 pts polarization)

This is a [3+2] cycloaddition between a dipole **G**, and a dipolarophile **H**. The reaction will be dictated by the electronic nature of the dipolarophile. Since **H** is electron deficient due to the methyl ester substituent, the reaction will proceed via the HOMO of **G** and the LUMO of **H**. The HOMO of **G** will be polarized towards the carbon; the LUMO of **H** will be polarized away from the ester thus dictating the regiochemical outcome. Since the C=C bond of **H** is in the *TRANS* configuration and the reaction is a concerted process the stereochemistry with regard to the methyl and CO₂Me ester will be *anti* in the product **I**.



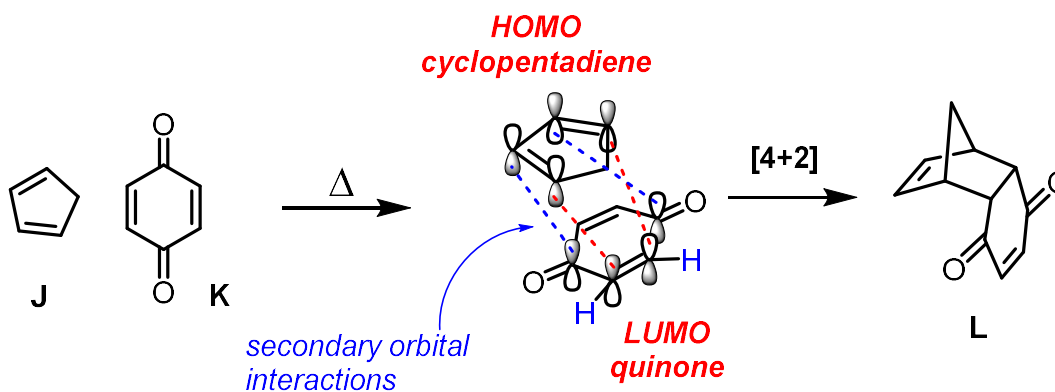


Cyclopentadiene (**J**) reacts with benzoquinone (**K**) upon gentle warming to give intermediate (**L**) which can undergo a photochemical reaction to give (**M**).

- a) Propose a structure for **L**. Justify the stereochemistry you draw for it using FMO theory.

(2 pts struct. + 2pts FMO HOMO/LUMO interaction + 2 pts endo secondary interactions)

The reaction is a [4+2] cycloaddition between electron rich diene **J** and electron poor dienophile **K**. The reaction will proceed via the HOMO of the diene **J** and the LUMO of the dienophile **K**. Secondary orbital interactions give rise to the kinetic and major product as the ENDO cycloadduct **L**.

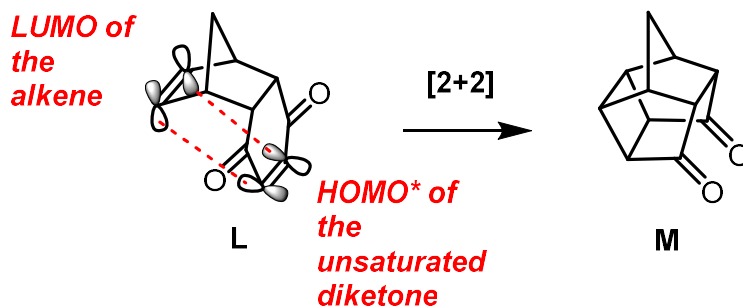


- a) Using FMO theory, explain why **L** is converted to **M** under photochemical conditions.

(2 pts HOMO*)

Under photochemical irradiation, α,β unsaturated diketone is excited such that one electron in the HOMO is promoted to the LUMO. The new FMOs under these conditions explain the formation of **M** via a [2+2] cycloaddition using the LUMO of

the α,β unsaturated diketone which is excited (HOMO*) and the LUMO of the alkene in the ground state.

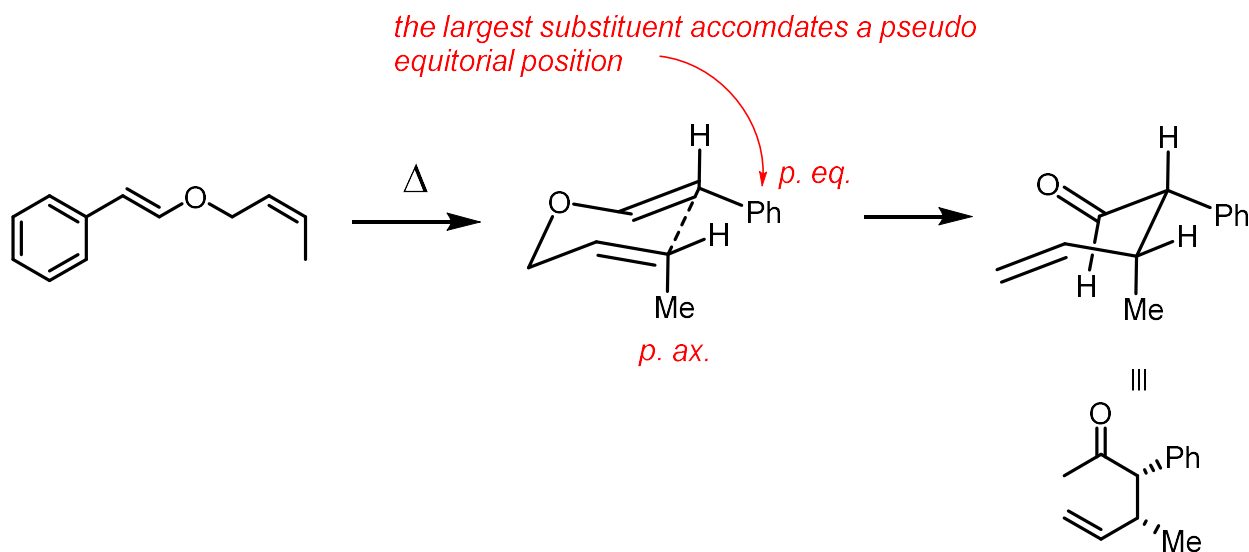


QUESTION 4

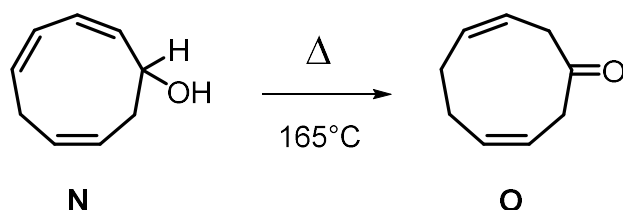
≈ 18 pts

For each of the following transformations, provide the type of pericyclic reaction involved (cycloaddition, electrocyclic reaction, sigmatropic rearrangement) and provide the stereochemical descriptor (exo/endo, conrotatory/disrotatory, suprafacial/antarafacial). Furthermore :

a) Provide the product of the following reaction :
(2 pts product, 2pts correct stereochemistry)

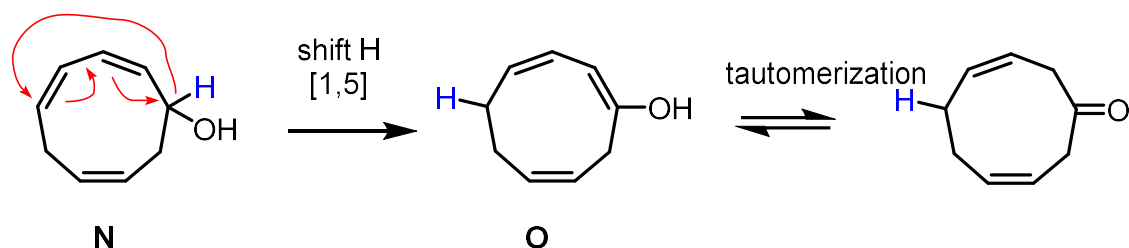


b) Provide a mechanism for the following reaction :



(2 pt reaction arrows, 1 pt [1,5] sigmatropic rearrangement 1 pt suprafacial)

This is a [1,5] sigmatropic rearrangement that proceeds via a suprafacially. A keto-enol tautomerization completes the mechanism.

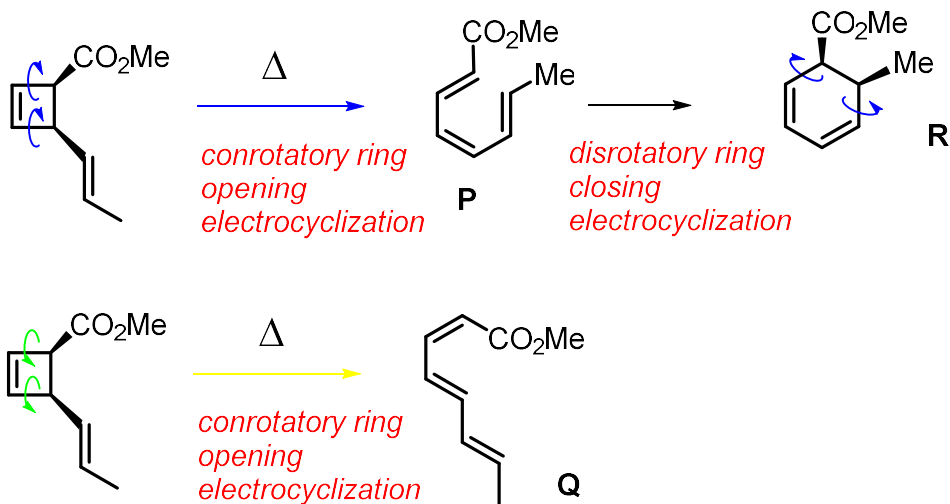


c) Provide the product (s) of the following reaction :

(2 pts diene, 2 pts other diene, 1pt electrocyclization., 1 pt conrotatory ring open, 2 pt correct cyclohexadiene product , 1pt electrocyclization., 1pt disrotatory ring closure)

Hint: There is no cycloaddition in (c)

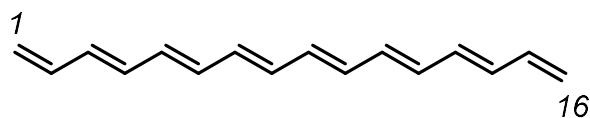
The cyclobutene ring undergoes a 4π conrotatory ring opening electrocyclization affording two triene products depending on the ring opening direction. One of the trienes **P** is adequately positioned to undergo a second 6π disrotatory ring closing electrocyclization to give cyclohexadiene **R**.



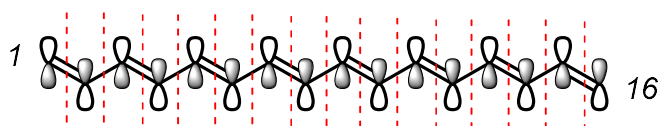
QUESTION BONUS

4 pts

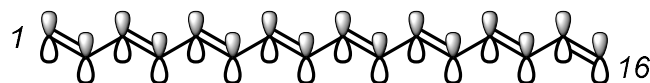
Consider the following polyene :



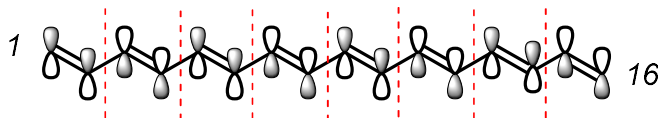
a) draw the highest energy MO



b) draw the lowest energy MO



c) draw the HOMO



d) draw the LUMO

