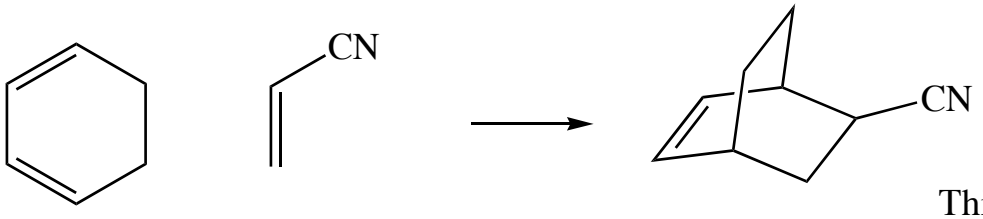
Exercise 83 - Orbital symmetry cycloaddn

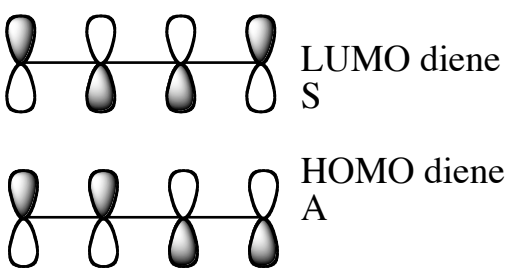
Question

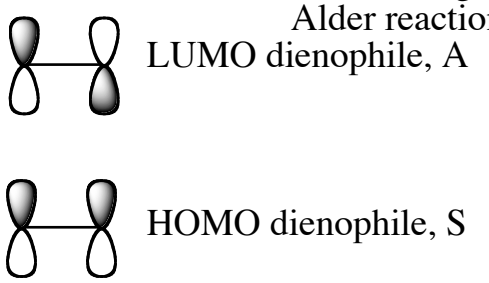
Give the structure of the products (ignore stereochemistry) expected in the following cycloaddition reactions. Which of the following are orbital symmetry allowed reactions?

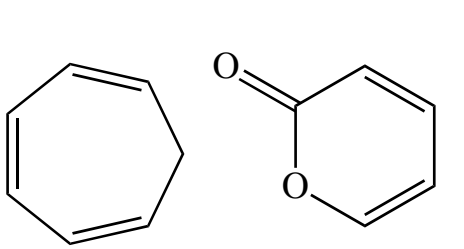


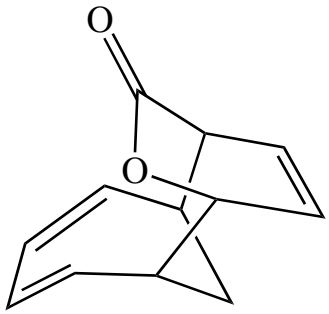
Allowed.

This is a regular Diels-Alder reaction.

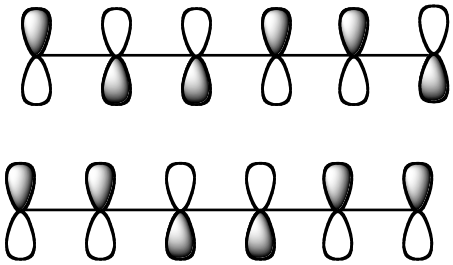


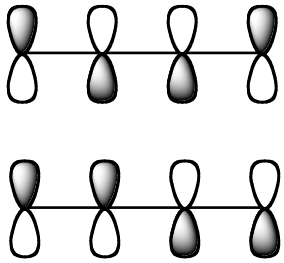


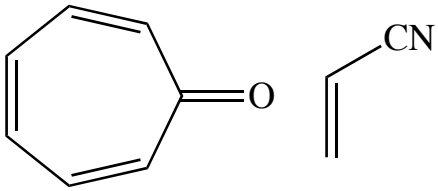


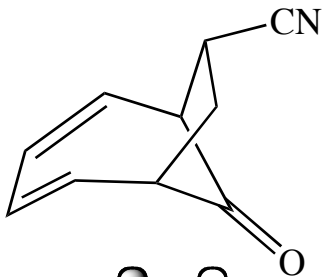


Allowed.

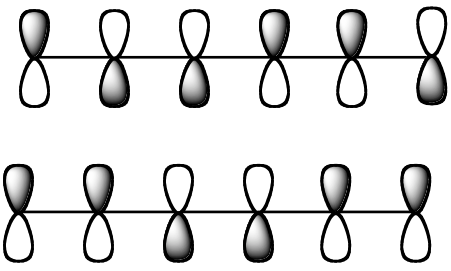


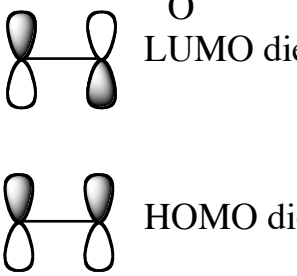


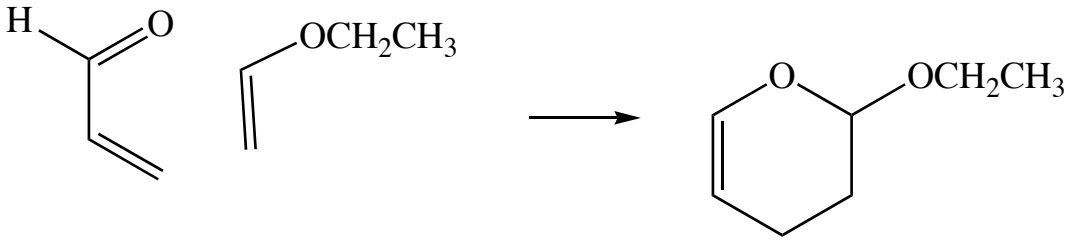




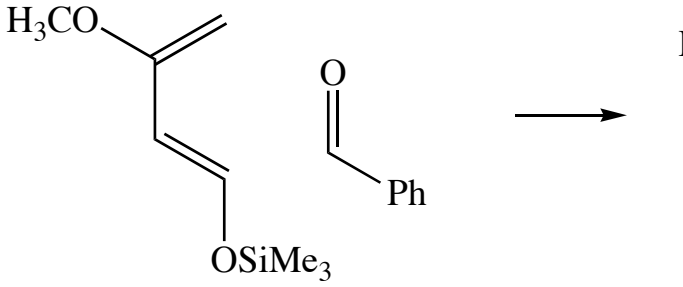
Forbidden

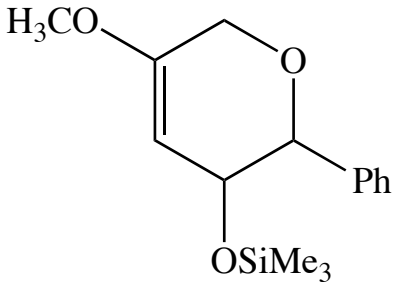






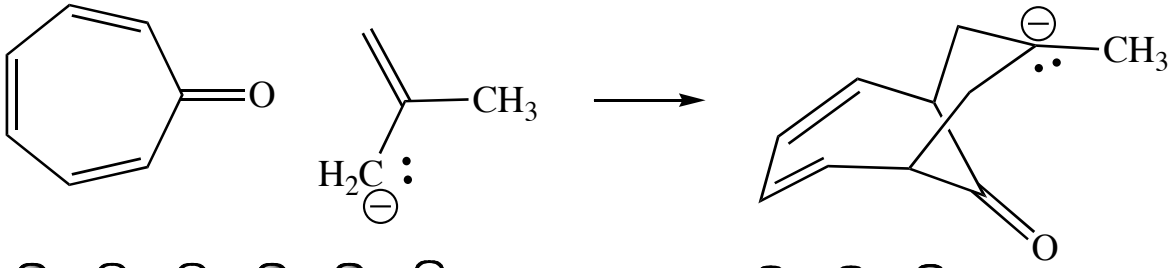
Allowed.



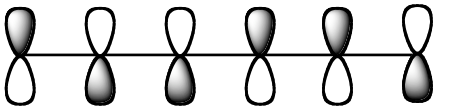


Allowed.

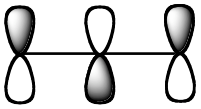
These are both 4 = 2 Diels-Alder reactions like the first question.



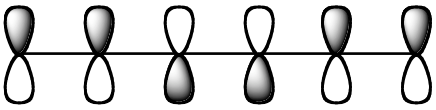
Allowed.



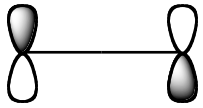
LUMO A



LUMO allyl with 4 pi electrons, S



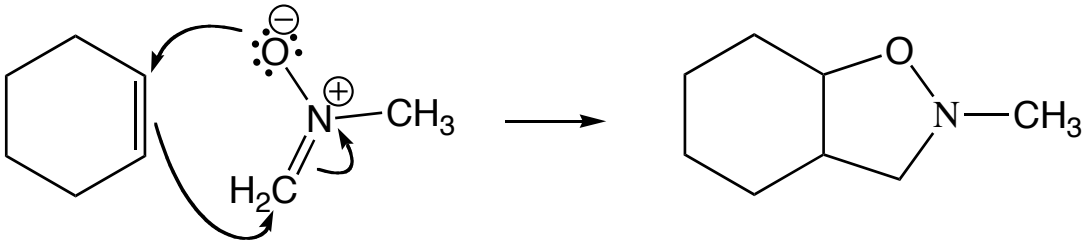
HOMO S



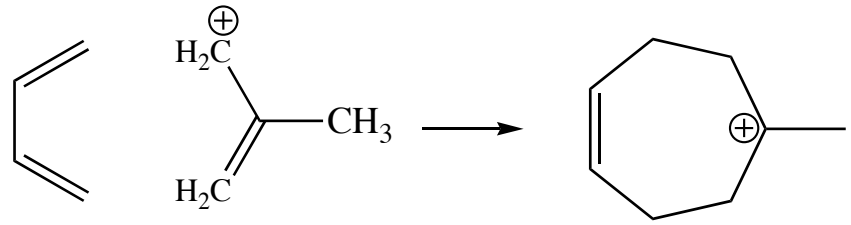
HOMO, A

Question

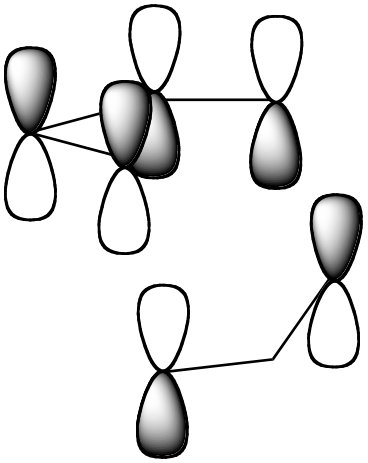
Nitrones, such as the one shown below, are isoelectronic with ozone. Give the structure of the product of this reaction.



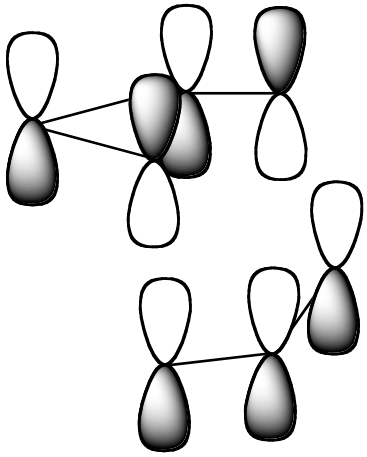
Question
The following is a cycloaddition reaction between butadiene and an allylic carbocation. By looking at both of the HOMO/LUMO interactions of the two species, show that the reaction is thermally allowed.



HOMO butadiene



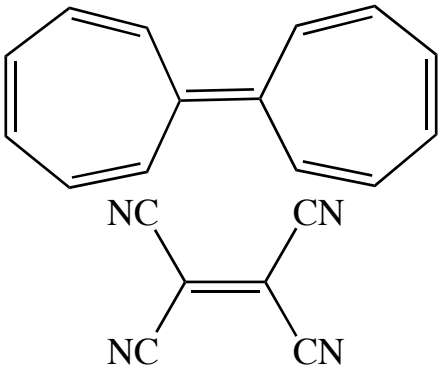
LUMO butadiene



LUMO allyl cation

HOMO allyl cation

Question
Would you expect the following reaction to be symmetry allowed? This is a 14π + 2 π electron process. I realize your tables don't extent to a 14 pi electron polyene, but you can still figure this out.



There are two ways to reason this out. If you look at your pi MO table, you'll note that for a two carbon pi system the HOMO is symmetric. For four it is antisymmetric, for six it is symmetric. By extension, 14 will be symmetric. Since the LUMO of ethylene is antisymmetric, this is not a symmetry allowed process.
The other way is to recognize, as we did in class, that when the total number of electrons involved is 4, the process is forbidden, 6 allowed, 8 forbidden, 10 allowed, 12 forbidden, 14 allowed and 16 forbidden. For n = an integer, those process with 4n+2 pi electrons will be allowe and 4n processes forbidden.