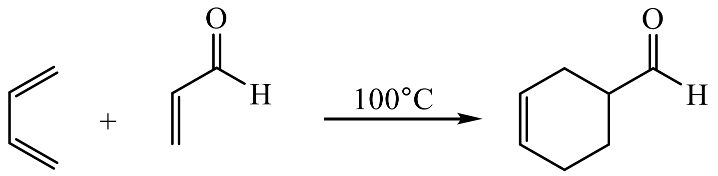
3:7) The Diels – Alder reaction:

α,β-Unsaturated carbonyl compounds undergoes an important and useful reaction with conjugated dienes, known as the Diels – Alder reaction. This is an addition reaction in which C-1 and C-4 of the conjugated diene system become attached to the doubly – bonded carbons of the unsaturated carbonyl compound to form a six – membered ring.

Note: *Conjugated diene must adopt the s-cis conformation.*

This reaction was discovered by Otto Diels and Kurt Alder which awarded a noble prize in chemistry in 1950 for their discovery.
The reaction takes place by heating a mixture of the conjugated diene and the dienophile to give a six membered ring.

e.g.



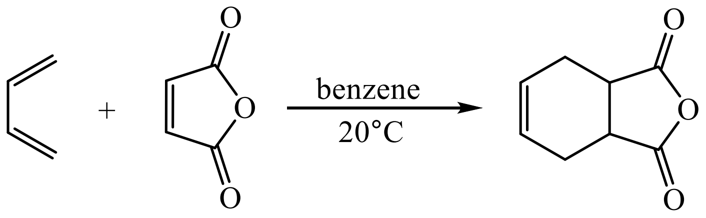
1,3-Butadiene   Acroline   3-Cyclohexene-1-carboxaldehyde

This reaction is useful not only because a ring is generated but also because it takes place so readily for a wide variety of reactants. The reaction occurs readily when the dienophile contains a strong electron withdrawing groups, this in contrast with the diene which activated by electron donating groups.

The reaction often takes place with the evolution of heat when reactant simply mixed together.

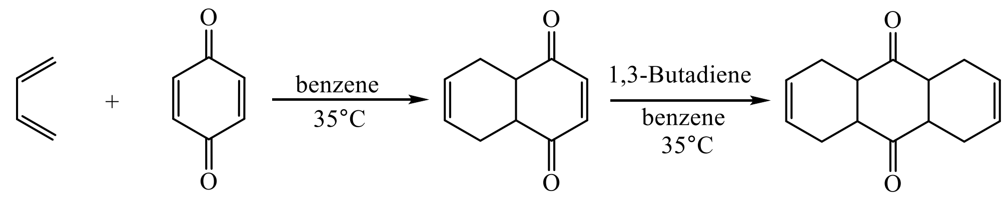
e.g.

1)



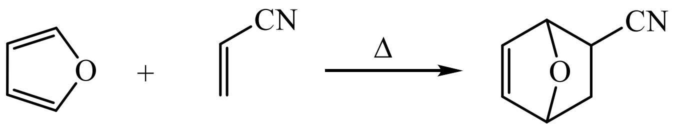
1,3-Butadiene   Maleic anhydride   Cis-1,2,3,6-tetrahydrophthalic anhydride

2)



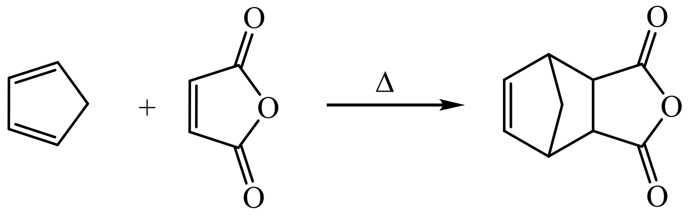
1,3-Butadiene p-Benzoquinone 5,8,9,10-Tetrahydro-1,4-naphthoquinone 1,4,5,8,11,12,13,14-Octahydro-9,10-anthraquinone

3)



Furan Acrelonitrile

4)

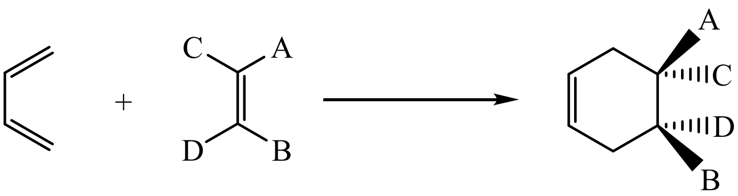


Cyclopentadiene

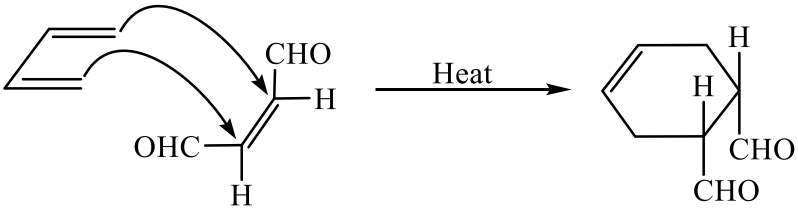
3:7:1) Stereochemistry of the Diels – Alder reaction:

In this reaction, the addition is stereospecifically syn (with respect to the dienophile). This means that groups that are cis in the alkene will be cis in the cyclohexene ring (A – B & C – D), and groups that are trans in the alkene will be trans in the cyclohexene ring (A – D & C – B).

<u>Note</u>: *The reaction is stereospecific and the addition of diene to dienophile occurs from one side (Syn addition).*



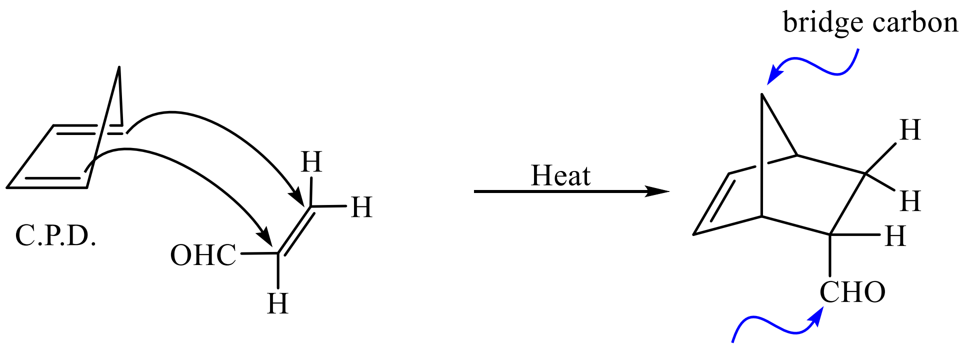
e.g.



Cis dienophile Syn adduct

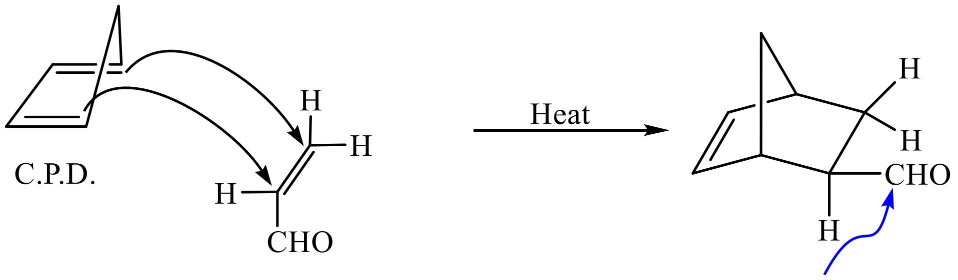
There are two possible ways that the diene approach from the dienophile (i.e. endo addition and exo addition), hence two products may be expected, (endo adduct and exo adduct).

e.g.



Endo addition
The CHO group is under the diene

This group is trans to the bridge carbon

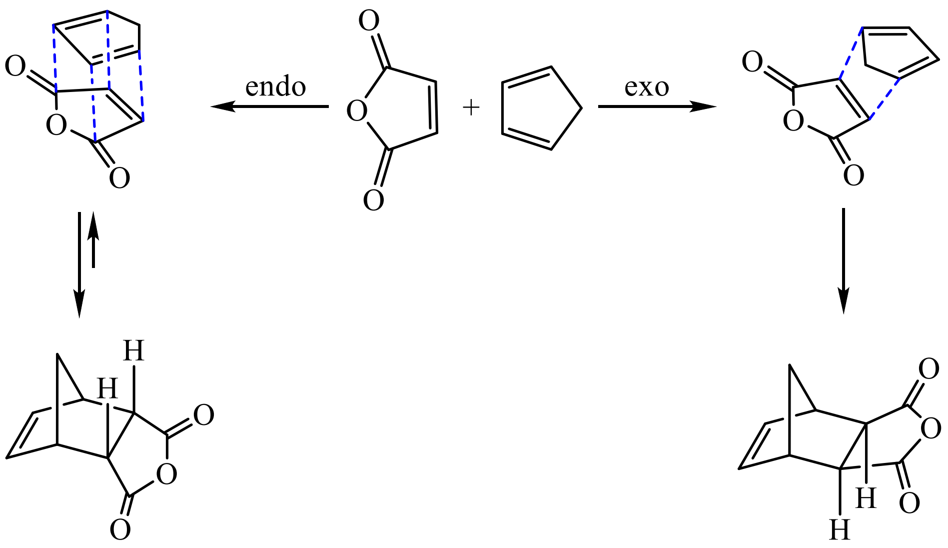


Exo addition
The CHO group lay out relative to the diene system

This group is cis to the bridge carbon

Note:

1- *C.P.D. = Cyclopentadiene*
2- *The endo mode of attack is the spatial arrangement of reactants in which the bulkier sides of the diene and dienophile lie one above the other, while in the exo mode of addition the bulkier side of one component is under the small side of the other.*
3- *The endo adduct is usually the major product because of stabilizing secondary orbital interactions in the transition state.*



Most of the time, the addition is predominately endo, since most of the addition product adopt the endo stereochemistry due to the overlap between π orbitals of the carbon – carbon bond that formed in the product with those of the dienophile, thus the energy required to reach the transition state will be decreased.