

Outline of the solution to Problem 3: A case of catalysis

10 marks

24 August, 2020

Two main reasons for greater yield of (i) as compared with (iii) are suggested below:

1. The role of the dienophiles:
(A) is a stronger dienophile due to presence of an electron withdraw group while (B) is a significantly weaker dienophile.
2. The role of MV:
 - (a) The MV is involved in encapsulation of the two reactant molecules as guest and aids in achievement of proper orientation for the cycloaddition reaction. It further potentially stabilizes the transition state for the reaction.
 - (b) The major contribution to the driving force for encapsulation is the stability provided to the guest molecules by $\pi - \pi$ interaction with the aromatic walls of the ligand. Thus, dienophile (A) is greatly stabilized by this interaction while (B) which does not have an aromatic substituent. Further, the non-planar cyclohexyl moiety which rotates freely about the C-N bond provides an additional orientational disorder which disallows proximity of the maleimide to the ligand walls in many orientations. Ultimately, incorporation of (B) inside MV is greatly affected.

To quantify the effect of dienophile strength on the yield, reactions (ii) and (iv) may be inspected –the yield ratio (ii) : (iv) is 1.25. So, the strength of the dienophile has quite a weak influence on the yield of the reaction (Reason 1 above).

In contrast, the yield ratio (i) : (iii) is 2. The dienophiles used are the same, so the much higher increment in yield must be attributed to the presence of MV and more stabilizing interactions with the substrates in reaction (i) (Reason 2 above). Another way to look at it would be to observe the yield ratios (i) : (ii) = 9 and (iii) : (iv) = 5.6. This indicates that the increase in yield due to presence of the catalyst is much greater for reactant (A) than (B) (Reason 2 (b) above).

The above line of reasoning goes to establish that Reason 2 above plays a much stronger role than Reason 1 in the discrepancy in yields of reactions (i) and (iii).