Diels Alder Stereochemistry Worksheet (ANSWERS)


![ENDO approach](image1)

![ENDO product](image2)


![ENDO approach](image3)

![ENDO ortho product](image4)

![ENDO ortho product](image5)

![EXO approach](image6)

![EXO ortho-para product](image7)

![EXO ortho-para product](image8)


The dienophile contains two unsaturated electron-withdrawing substituents: CO$_2$Me and NO$_2$. We normally expect NO$_2$ to be a more powerful electron acceptor, and this squares with most of the reaction data. Focusing on NO$_2$, we see that both products are ortho (the bottom case where X = OMe and Y = OSiMe$_3$ can be viewed as combined ortho-para), and the preferred product is endo (except for the last case).

In an *inverse electron demand* reaction, you need to look for electron-*donating* substituents on the dienophile (OSiMe₃) and electron-*withdrawing* substituents on the diene (C=O).

The diene and dienophile, and their respective electron-poor/rich sites are shown below:

The observed products are *ortho*. The authors claim that most of the dienophiles give *endo* products. They must be referring to the position of the OSiMe₃ substituent since this group ends up *cis/endo* to the alkene. This outcome makes sense since OSiMe₃ is an electron-*donor* substituent and this is an inverse electron domain reaction.


Don’t be fooled by CO₂Et in the diene. The electron-withdrawing “substituent” is the C=O bond (or, more usefully, the O atom). 4 and 5 are both *ortho*. The *endo rule* predicts the formation of 4. I arrived at this conclusion by assuming that the rule predicts the stereochemistry of electron-*donating* dienophile substituents in *inverse electron demand* reactions (see previous example).