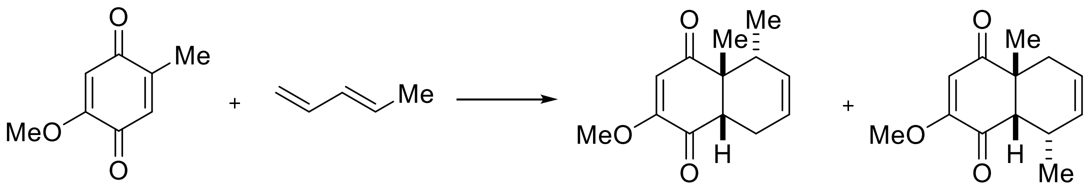
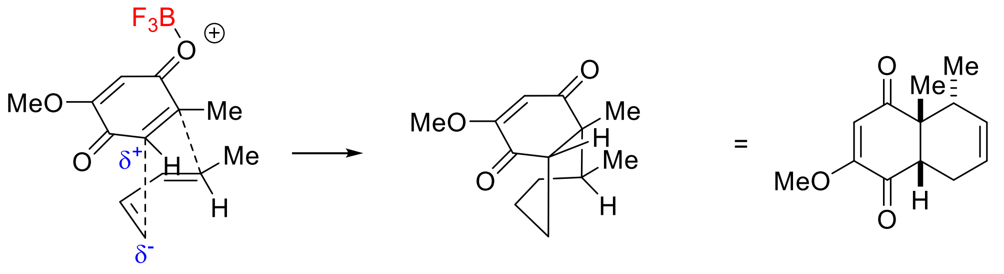
# SR2024 - POW 6 - Solutions

## I)

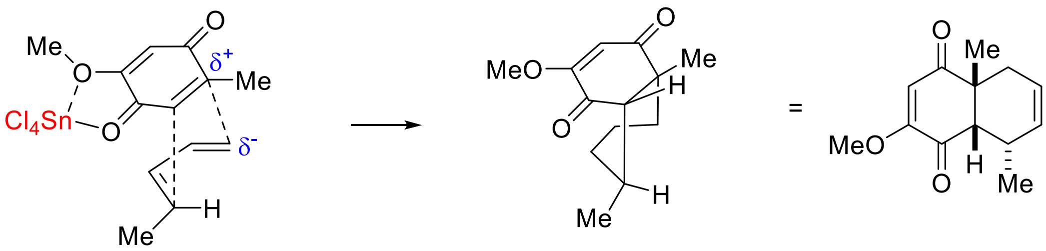
*The following example of a Diels-Alder reaction shows an interesting selectivity switch when the condition are changed. Try to explain this selectivity taken the discussed concepts and the differences of the two Lewis-Acids into account?*



| | | |
|---|---|---|
| conditions: | 100 °C | 1:1 |
| | $BF_3{\bullet}OEt_2$, -20 °C | 80:20 |
| | $SnCl_4$, -20 °C | 5:95 |



*as major product*

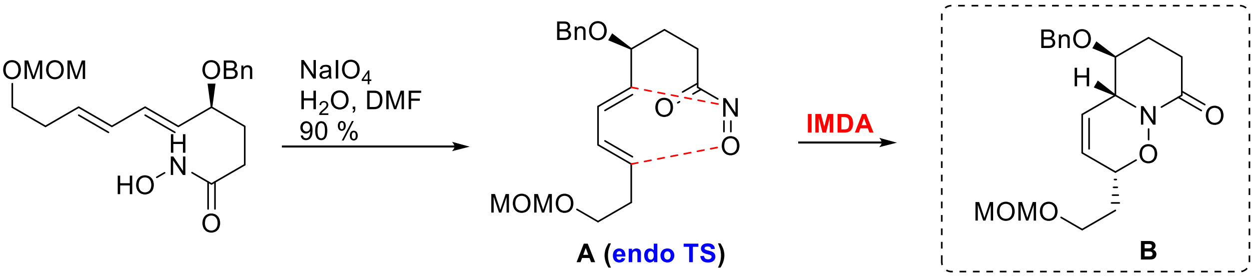


*as major product*

Without a catalyst, the electronic influence is in nearly symmetrical, hence there is no bias for a selectivity. $BF_3$ has a single free coordination site and prefers to coordinate to the ketone without the methoxy group (space is more accessible). $SnCl_4$ as bidentate Lewis-acid can coordinate to both the ketone **and** the methoxy group. The presence of the Lewis acid makes the corresponding olefin in beta position much more electrophilic and determines the regioselectivity.

## II)

*What are the structures of **A** and **B**, explain as well the stereochemistry?*



**A (endo TS)**

**B**

The periodate oxidizes the hydroxamic acid to the acyl-nitroso species **A**. Acylnitroso compounds are unstable and are thus very difficult to isolate. However, they are very reactive dienophiles for the Diels-Alder reaction and undergo a fast in situ intramolecular Diels-Alder (IMDA) cycloaddition to give product **B**.