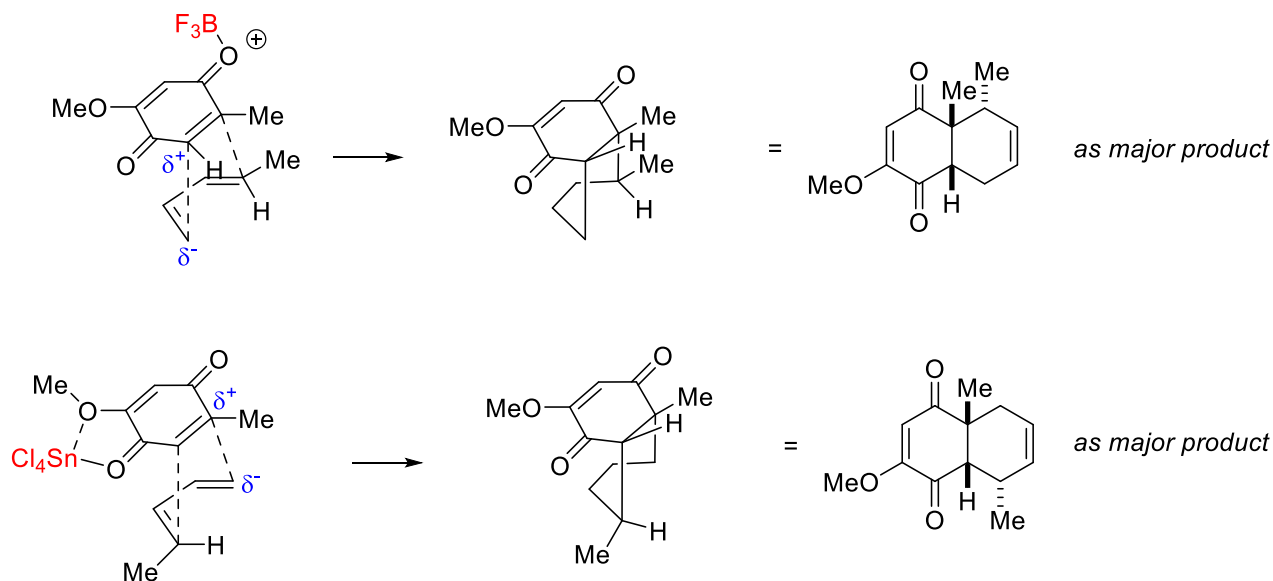
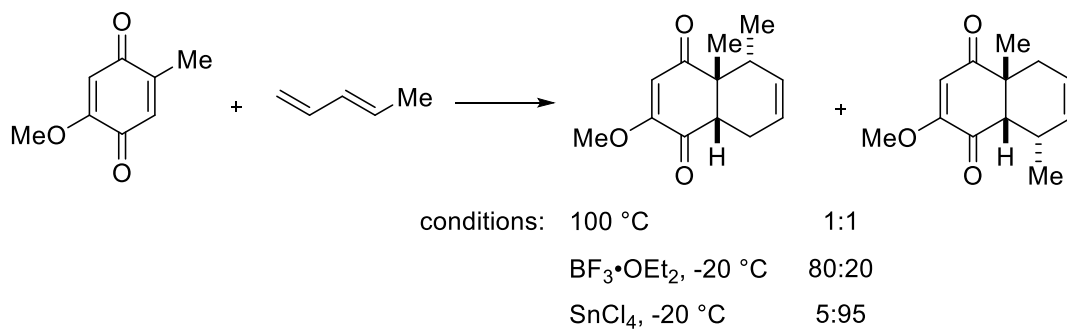


SR2025 - POW 6 - Solutions

I)

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

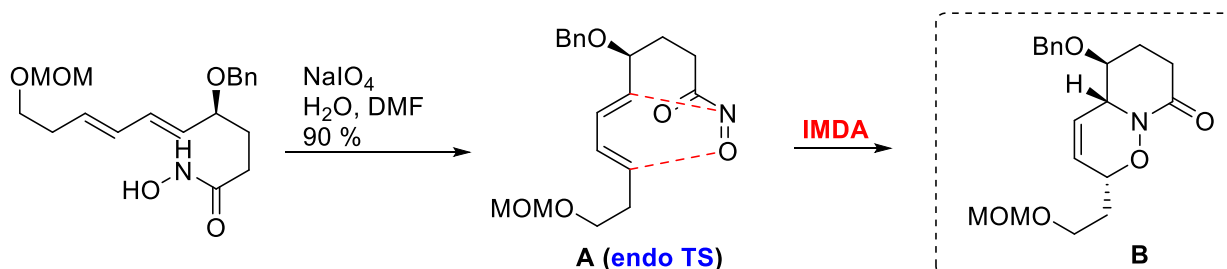


Without a catalyst, the electronic influence is in nearly symmetrical, hence there is no bias for a selectivity.

BF₃ has a single free coordination site and prefers to coordinate to the ketone without the methoxy group (space is more accessible). SnCl₄ 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?



The periodate oxidizes the hydroxamic acid to the acyl-nitroso species **A**. Acyl-nitroso 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**.