Problem Set 4 Solutions

(1)

This alkene is not reactive enough; need dienophilic equivalent

Some potential dienophilic equivalents:

1) Wittig
2) Hydrogenation

The reaction proceeds suprafacially with respect to the diene, giving the stereochemistry shown.
(7) Exo epoxidation on less hindered face

OAc \[\rightarrow\] EWG

Cyclopentadiene + Allyl Ester \[\xrightarrow{\text{Et}_2\text{O}, \text{rt}}\] Ketone \[\xrightarrow{\text{mCPBA}, \text{CH}_2\text{Cl}_2}\] Epoxide

Baeyer-Villiger to give ester and epoxidation in one step!

(8) Could be from dienophile

NHCO\text{t-Bu} \[\rightarrow\] Alkene + Nitrile

Problem: how to control the stereochemistry at the amine when alkene is produced in this position?

Solution: can control stereochemistry at the adjacent carbon and then use 1,3 O→N chirality transfer.
(10) The creation of a mixture of products favoring one enantiomer over another from a racemic mixture in the absence of chiral reactants is impossible. In the case of the "asymmetric synthesis" of santonin from 2-methyl-2-formylcyclohexanone, the optical rotation is likely due to the presence of impurities in the sample.