# Conjugated dienes: the Diels-Alder reaction

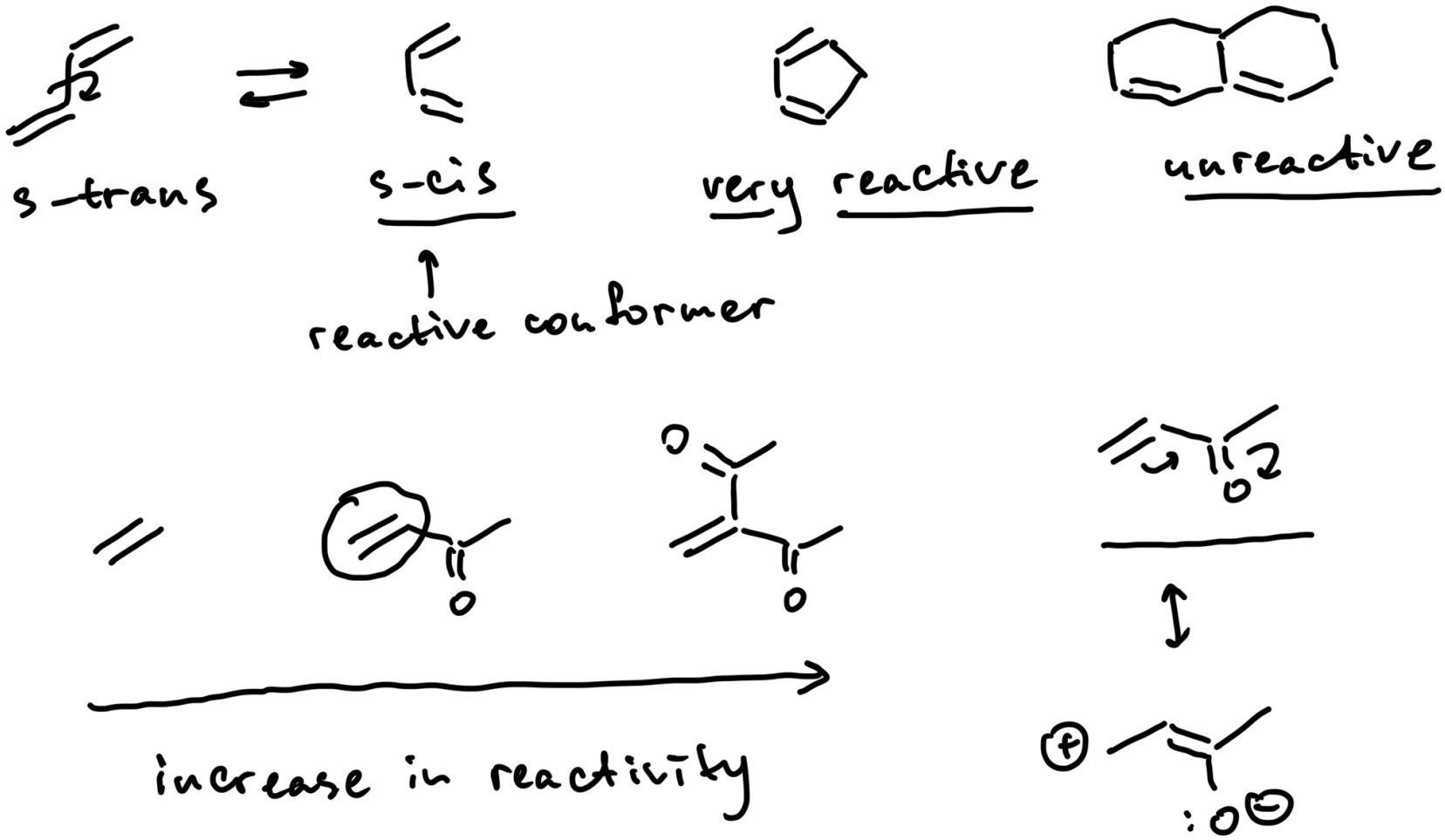
Diene and dienophile. Mechanism. Thermodynamics

diene dienophile

- three π bonds are broken
- make two σ bonds and one π bond
- thermal
- concerted

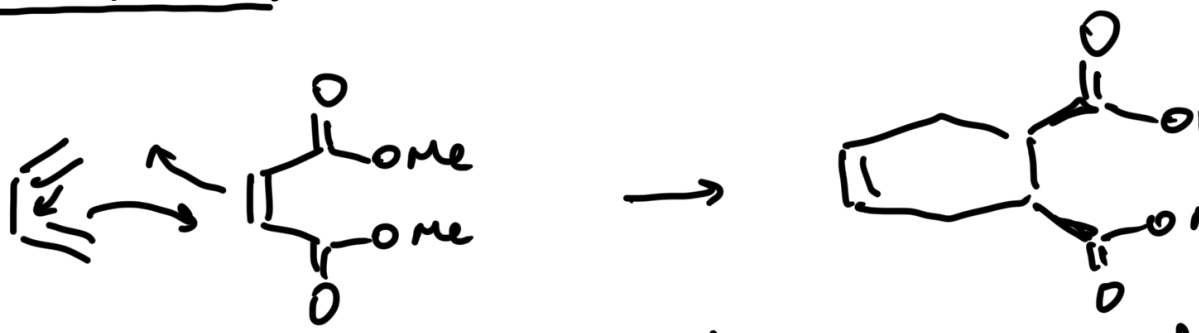
# Conjugated dienes: the Diels-Alder reaction

Conformation of diene and structure of dienophile



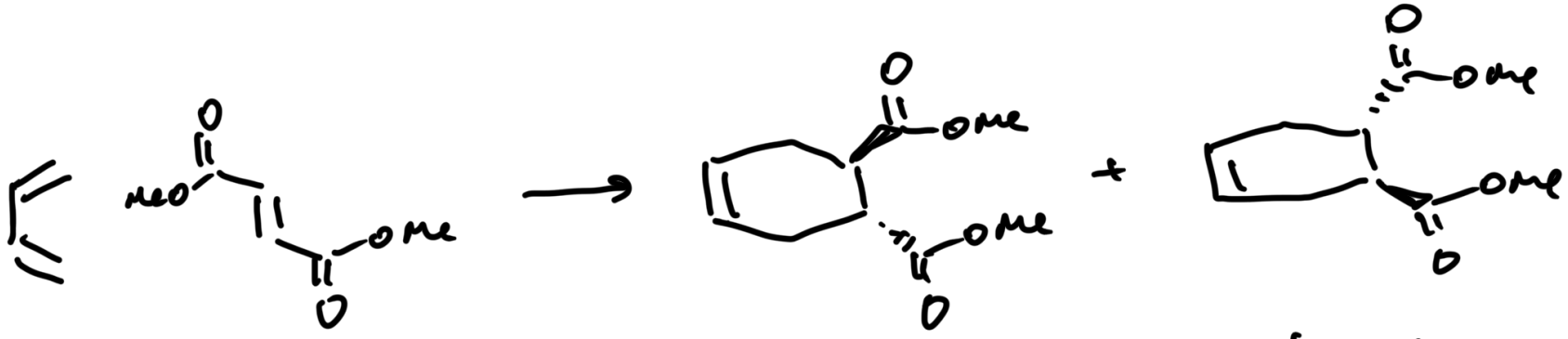
# Conjugated dienes: the Diels-Alder reaction

Stereospecificity



maleic acid diester
(cis alkene)

cis product only product



fumaric acid diester
(trans alkene)

trans

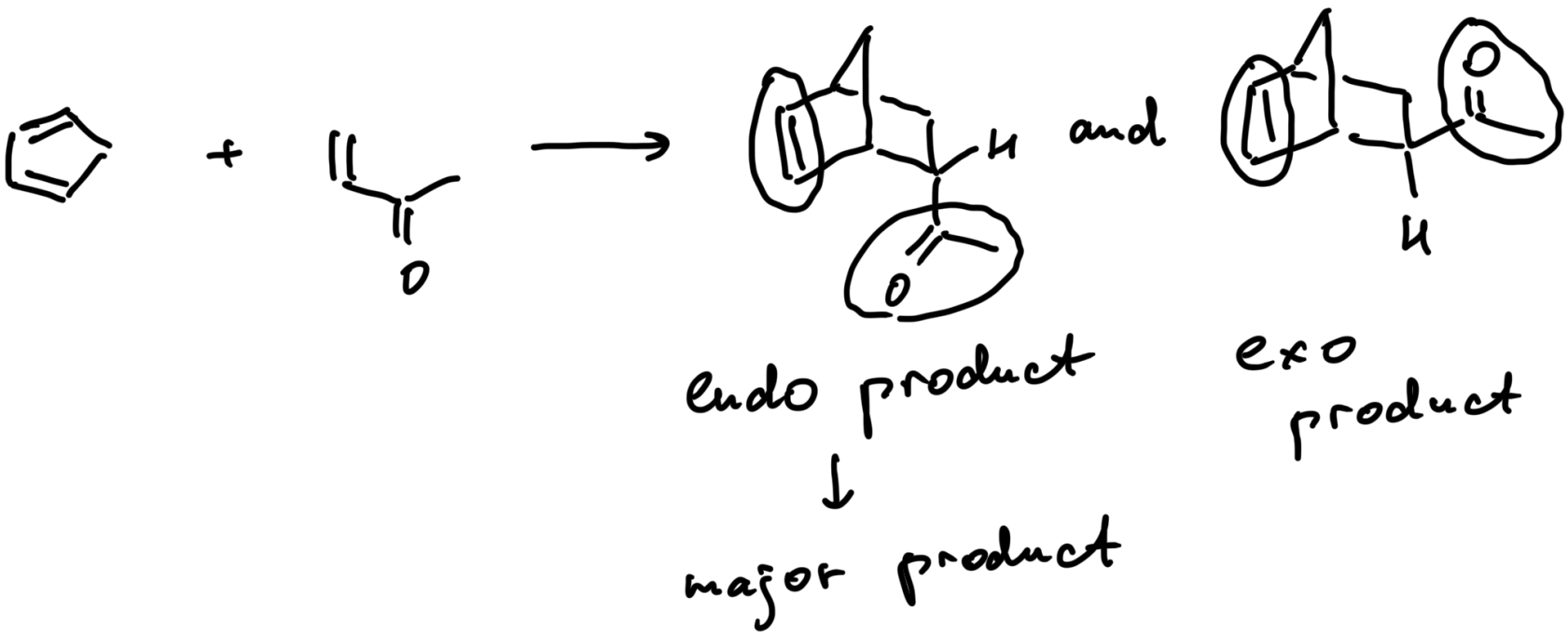
+

trans

enantiomers

# Conjugated dienes: the Diels-Alder reaction

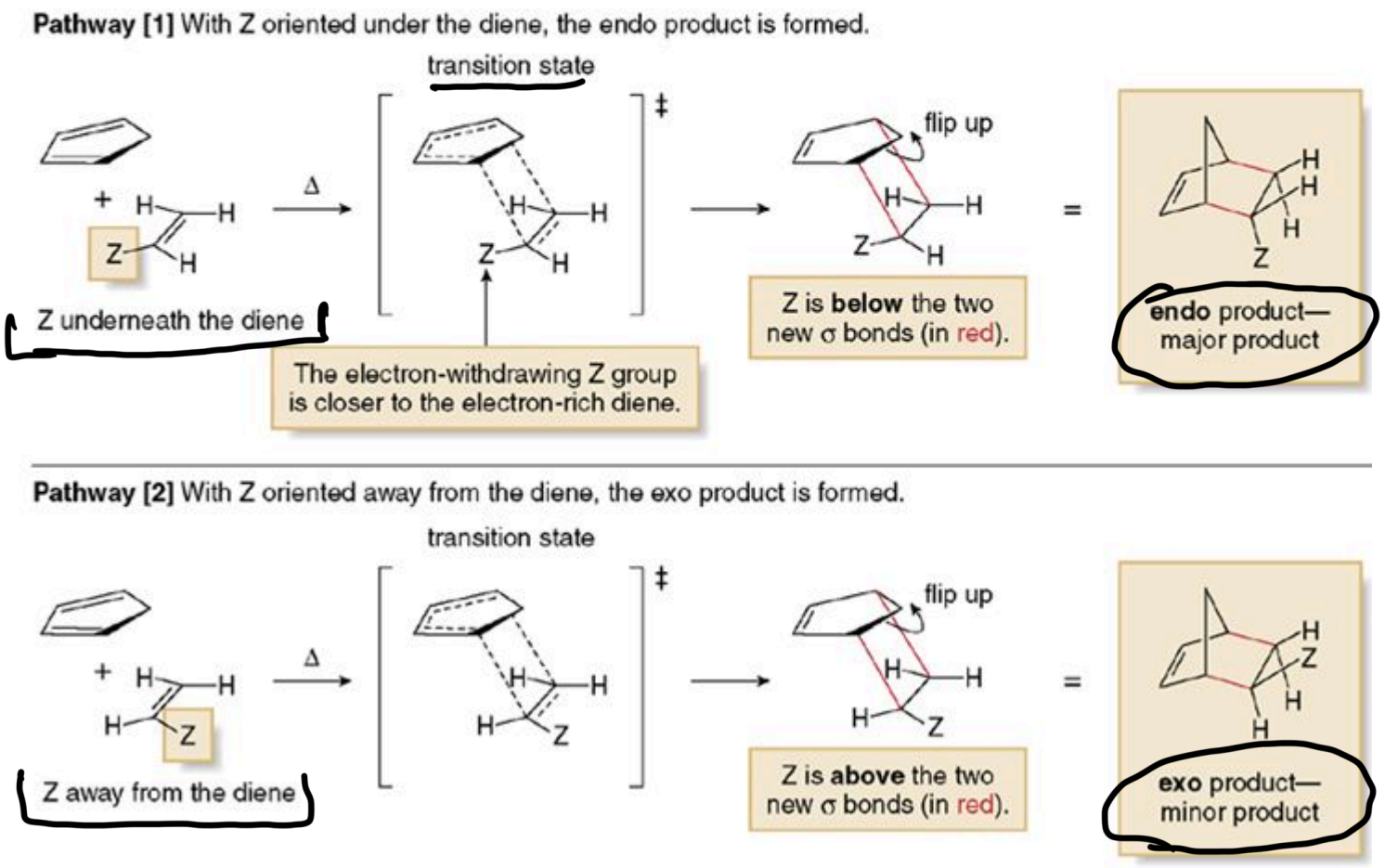
Stereoselectivity. Alder's endo rule



# Conjugated dienes: the Diels-Alder reaction

Stereoselectivity. Alder's endo rule. Further reading

Chapter 14 → read



# Final

- Ch. 7: nucleophilic substitution reactions
- Ch. 8: elimination reactions
- Ch. 9: alcohols, ethers and related compounds
- Ch. 10: alkenes
- Ch. 11: alkynes
- Ch. 12: oxidation and reduction
- Ch. 15: radical reactions
- Ch. 16: conjugation, resonance, and dienes

# Ch. 7

- Sections to prioritize: 7.6 – 7.15, 7.17, 7.18
- Lectures 1 – 5 (parts of)
- Including (but not limited to): mechanisms of $S_N2$ and $S_N1$ reactions; effect of the alkyl group; effect of the leaving group; effect of the nucleophile; effect of the solvent; predicting the mechanism of nucleophilic substitution in specific cases; nucleophilic substitution in synthesis

# Ch. 8

- Sections to prioritize: 8.1 – 8.11 (entire chapter)
- Lectures 5 – 8 (lecture 8 also contains some good problems for $S_N1$ vs. $S_N2$ vs. E1 vs. E2)
- Including (but not limited to): stability of alkenes; mechanisms of E2 and E1 reactions; effects of the alkyl group; effect of the leaving group; effect of the base; effect of the solvent; anti periplanar arrangement in E2; Zaitsez rule; $S_N1$ vs. E1. vs $S_N2$ vs. E2

# Ch. 9

- Sections to prioritize: 9.7 – 9.9, 9.11 – 9.16
- Lectures 9 – 14 (parts of)
- Including (but not limited to): synthesis of alcohols, ethers, epoxides, thiols, sulfides; dehydration of alcohols in acid, mechanism; carbocation rearrangements; conversion of alcohols to alkyl halides with HX, $SOCl_2$, and $PBr_3$, mechanisms; synthesis and reactions of tosylates; angle strain and reactions of epoxides with strong nucleophiles and with acids, mechanisms

# Ch. 10

- Sections to prioritize: 10.7 – 10.18
- Lectures 14 (parts of) – 17 (parts of)
- Including (but not limited to): synthesis of alkenes via elimination; hydrohalogenation reactions, mechanism and selectivity; Markovnikov's rule; hydration reactions, mechanism and selectivity; halogenation reactions, mechanism and selectivity; halohydrin formations, mechanism and selectivity; hydroboration–oxidation reactions and selectivity; alkenes in synthesis

# Ch. 11

- Sections to prioritize: 11.5 – 11.12
- Lectures 17 (parts of) – 19 (parts of)
- Including (but not limited to): synthesis of alkynes via elimination, alkylation of acetylide anions; acidity of terminal alkynes; hydrohalogenation reactions, mechanism (see lecture 18) and selectivity; halogenation reactions, mechanism and selectivity; hydration reactions, mechanism and selectivity; hydroboration–oxidation reactions and selectivity; mechanism of tautomerization; alkynes in synthesis

# Ch. 12

- Sections to prioritize: 12.3, 12.5 – 12.10, 12.12
- Lectures 19 (parts of) – 22 (parts of)
- Including (but not limited to): hydrogenation of alkenes and reactivity trends; hydrogenation of alkynes to alkanes and *cis*-alkenes; reduction of alkynes to *trans*-alkenes; reduction of polar C–X sigma bonds; epoxidations, mechanism and selectivity; syn and anti dihydroxylations, mechanism and selectivity; oxidative cleavage of alkenes; oxidation of alcohols with Cr(~~IV~~ VI), mechanism and selectivity

# Ch. 15

- Sections to prioritize: 15.1 – 15.8, 15.10, 15.13
- Lectures 22 (parts of) – 23
- Including (but not limited to): stability of alkyl radicals; radical chlorination and bromination of alkanes, mechanism and selectivity; allylic brominations, mechanism and selectivity

# Ch. 16

- Sections to prioritize: 16.1 – 16.6, 16.8, 16.10, 16.11
- Lecture 24
- Including (but not limited to): resonance, resonance stabilization, contributions to resonance hybrids; updated stability of carbocations; electrophilic addition to conjugated dienes; 1,2- and 1,4-addition products, mechanism; kinetic vs. thermodynamic products