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Chapter 16 (Klein) Summary: Conjugated Dienes

I) Conjugated Dienes (16.1, 16.2)

A) $\Delta H_{hydrogenation}$ relates to stability of diene

B) Molecular Orbital (MO) Theory to describe conjugated systems (16.3)

II) Allylic reactivities and resonance

A) Resonance-stabilized carbocations

B) Resonance-stabilized radicals and free-radical halogenation with NBS (10.7)

C) Allylic S_N1/S_N2 is favored, like benzylic S_N1/S_N2 (17.6)

III) Electrophilic Additions (HX or X_2) to conjugated dienes (16.4) ***SkillBuilder 16.1***

A) Markovnikov addition gives <u>allylic carbocation</u> intermediate

B) 1,2-addition

a) kinetic product (favored in cold reaction conditions)

b) has more stable T.S. (allylic 2˚ δ+) and lower E_a so <u>faster</u> reaction

C) 1,4-addition

a) thermodynamic product (favored with addition of heat)

b) more stable product (internal pi bond)

c) heat allows equilibration of product mixture (reversible reaction)

D) Kinetic vs. Thermodynamic control (16.5) ***SkillBuilder 16.2***

IV) Diels-Alder Reaction: [4+2] cycloaddition reaction gives cyclohexene products (16.7)

A) dienophile E^+

i) alkene or alkyne

ii) typically bears EWG to be electron-poor (–COR, –CN, $–NO_2$)

B) diene Nu:

i) often bears EDG to be electron-rich (–OR, –OTMS)

ii) must have s-cis conformation

iii) cyclic dienes give bridges, bicyclic products

C) Stereochemistry

i) endo bicyclic products usually favored

ii) stereochemistry of starting materials is retained ***SkillBuilder 16.3***

D) Regiochemistry: 1,2- or 1,4-substitution patterns favored over 1,3-disubstituted

V) MO Theory to predict outcomes of pericyclic reactions, Woodward-Hoffmann rules (16.8)

A) HOMO-LUMO interactions, and conservation of orbital symmetry

B) [4+2] cycloadditions are *thermally allowed*

C) [2+2] cycloadditions are *photochemically allowed* (involves excited HOMO)

Read on your own: Chemistry of color and vision (16.12, 16.13)

Skip sections: Other pericyclic reactions (16.9, 16.10), UV Spectroscopy (16.11)

Chapter 16 Suggested Problems: see syllabus