

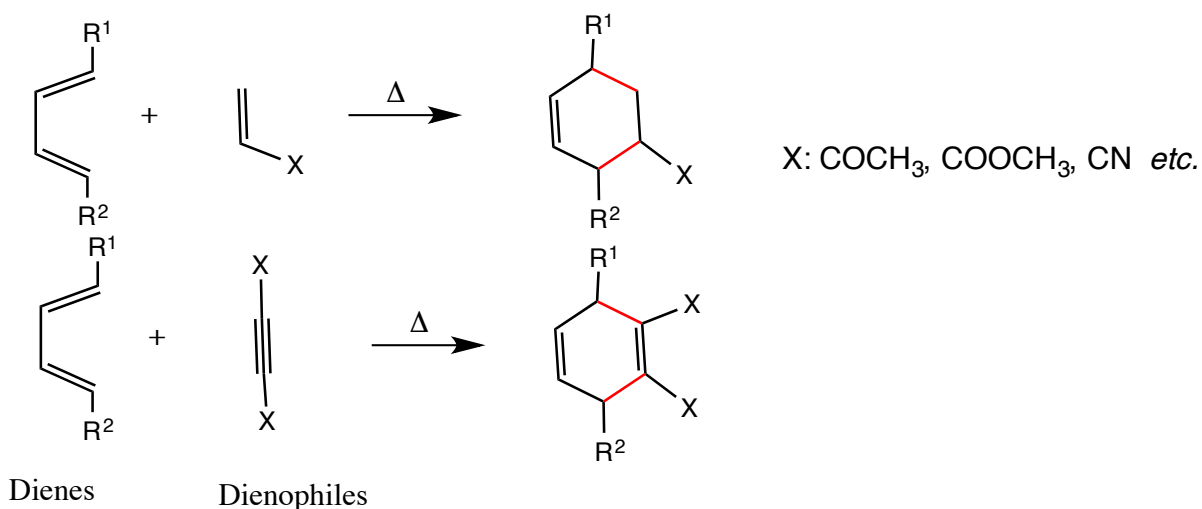
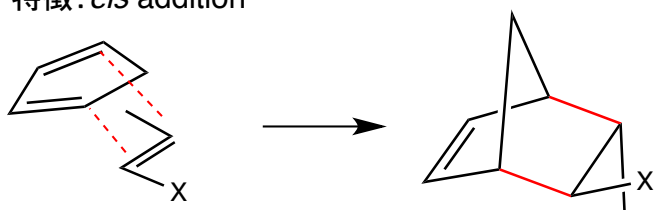
20 周辺環状反応 Pericyclic Reactions

20.1 共通の特徴

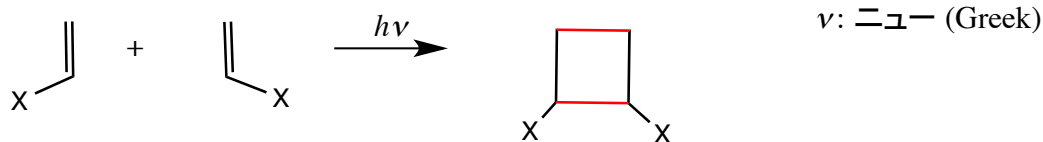
- ・熱反応または光反応 Thermal or photo reactions
- ・一段階(中間体なし) One step (no reaction intermediate)
- ・複数の箇所ですべて同時に起こる(協奏反応 Concerted reaction)

20.2 Cycloaddition Reactions 環化付加反応

(1) Diels-Alder Reaction [4+2]

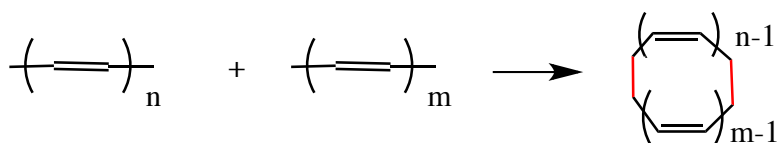
特徴: *cis* addition

(2) Photo Cycloaddition of Alkenes [2+2]



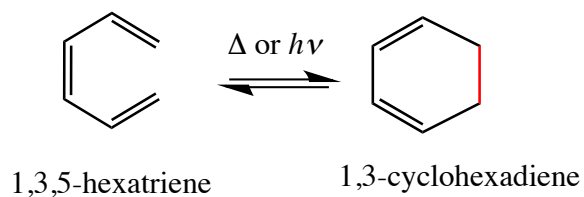
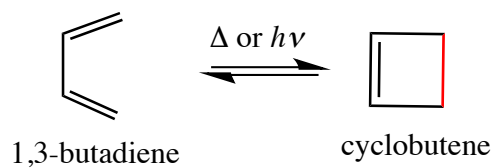
(参考)

(3) General Rule for [n+m] cycloadditions

 $n + m = 4n + 2$: Thermal Reactions (Δ) $n + m = 4n$: Photo Reactions ($h\nu$)

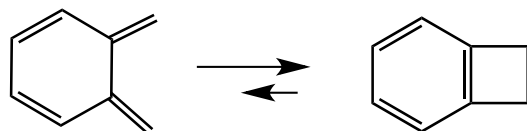
20.3 Electrocyclic Reactions 電子環状反応

Cyclization of Conjugated Polyenes and its Reverse Reaction

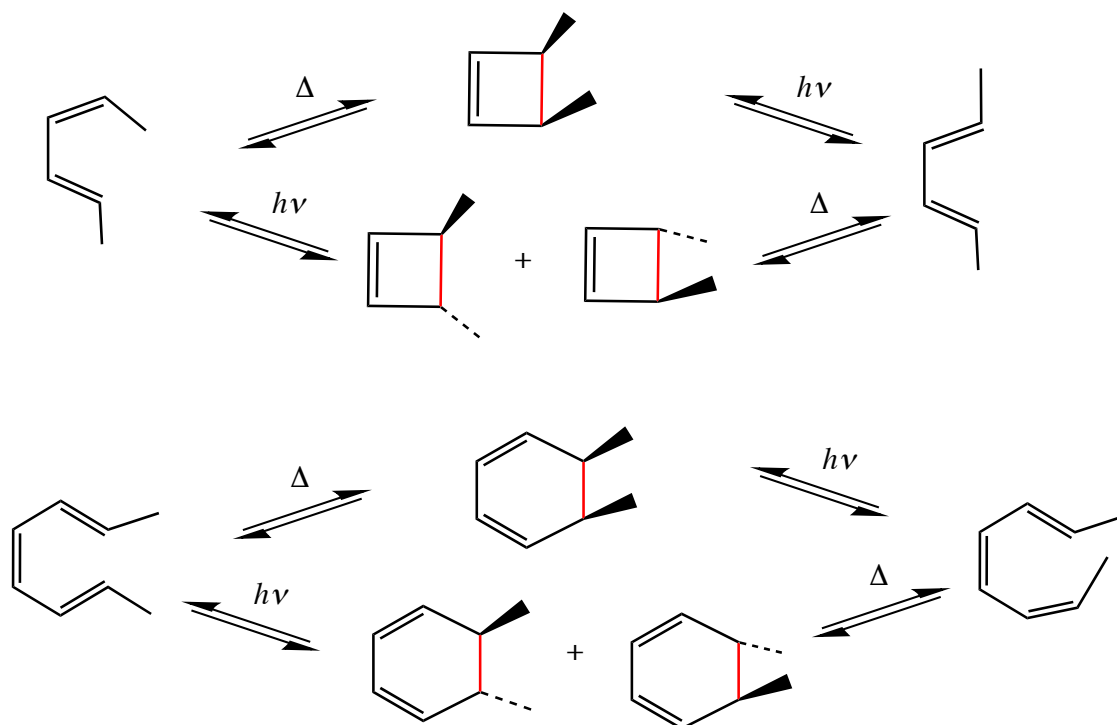


安定な生成物を与えるほうに平衡は片寄る

ex)



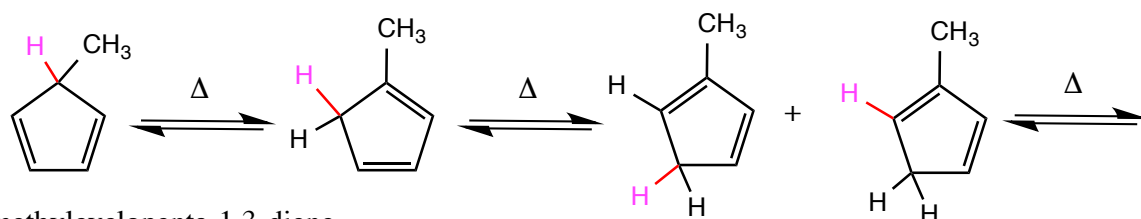
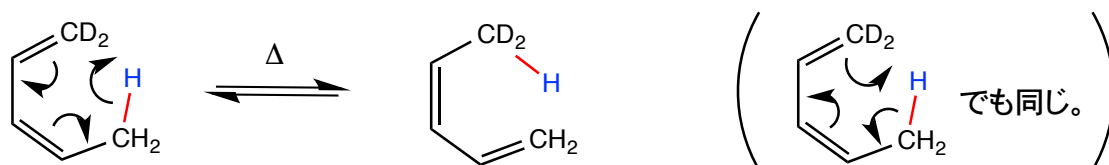
(参考) Stereoselectivity 立体選択性



20.4 Sigmatropy Rearrangement シグマトロピー転位

Intramolecular exchange of σ Bonds 分子内での σ 結合の組み替え

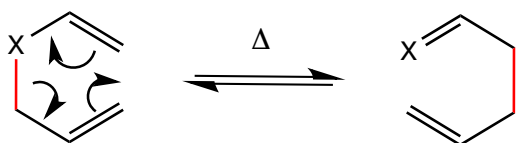
(1) [1,5] Rearrangement



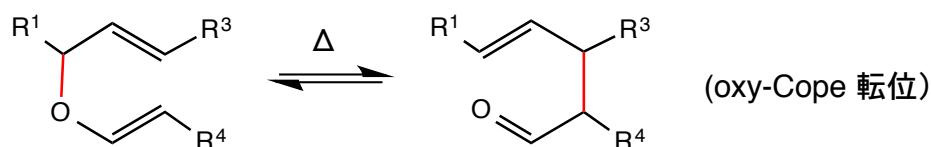
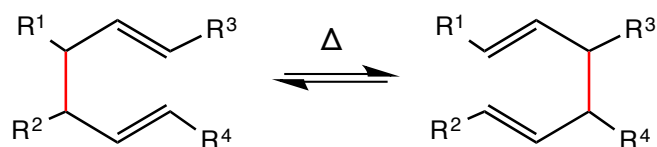
5-methylcyclopenta-1,3-diene

Hは環のどのC原子にも移動できる

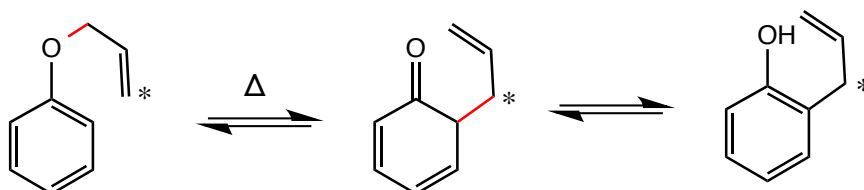
(2) [3,3] Rearrangement



(例) Cope 転位



(例) Claisen 転位



For further background, refer to "Woodward-Hoffman's Rule"