

M.Sc. Semester-IV
Core Course-9 (CC-9)
Synthetic Organic Chemistry



II. Pericyclic Reactions
10. Cope Rearrangement



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II Pericyclic Reactions 20 Hrs

Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3-butadiene, 1, 3, 5-hexatriene, allyl system, Classification of pericyclic reactions. FMO approach, Woodward-Hoffman correlation diagram method and PMO approach for pericyclic reaction under thermal and photochemical conditions.

Electrocyclic reactions: Conrotatory and disrotatory motion, $4n$ and $(4n+2)$ systems, Cycloaddition reaction: $[2+2]$ and $[4+2]$ cycloaddition reaction, Cycloaddition of ketones, Secondary effects in $[4+2]$ cycloaddition. Stereochemical effects on rate of cycloaddition reaction, Diels-Alder reaction, 1,3-dipolar cycloaddition, Chelotropic reaction, The Nazarov reaction.

Sigmatropic rearrangement: Suprafacial and antarafacial shift involving H and carbon-moieties, Peripatetic cyclopropane bridge, Retention and inversion of configuration, $[3,3]$ -, $[1,5]$ -, $[2,3]$ -, $[4,5]$ -, $[5,5]$ -, and $[9,9]$ -Sigmatropic rearrangements, Claisen rearrangements (including Aza-Claisen, Ireland-Claisen), Cope rearrangements (including Oxy-Cope, Aza-Cope), Sommelet-Hauser rearrangements, Group transfer reaction, Ene reaction, Mislow - Evans rearrangement, Walk rearrangement.

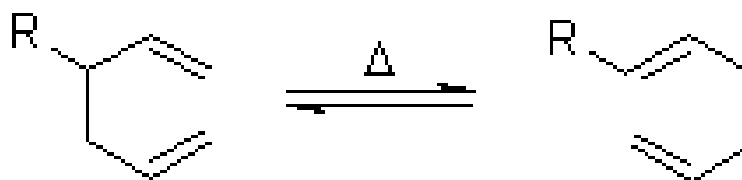
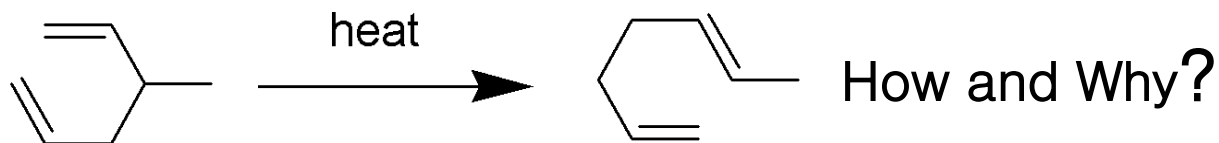
Coverage:

1. Cope Rearrangements
2. Oxy- Cope Rearrangements

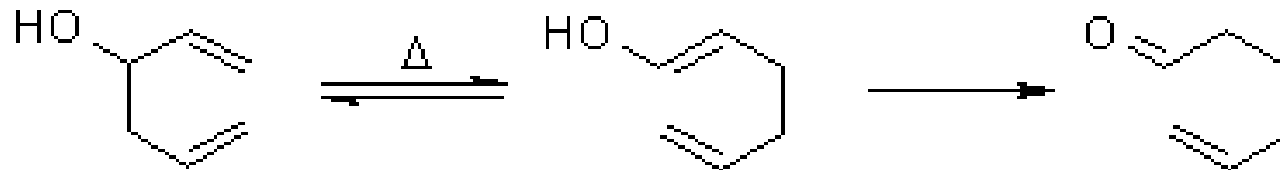
Cope Rearrangements : [3, 3] Sigmatropic Rearrangement



Arthur Clay Cope
1909-1966



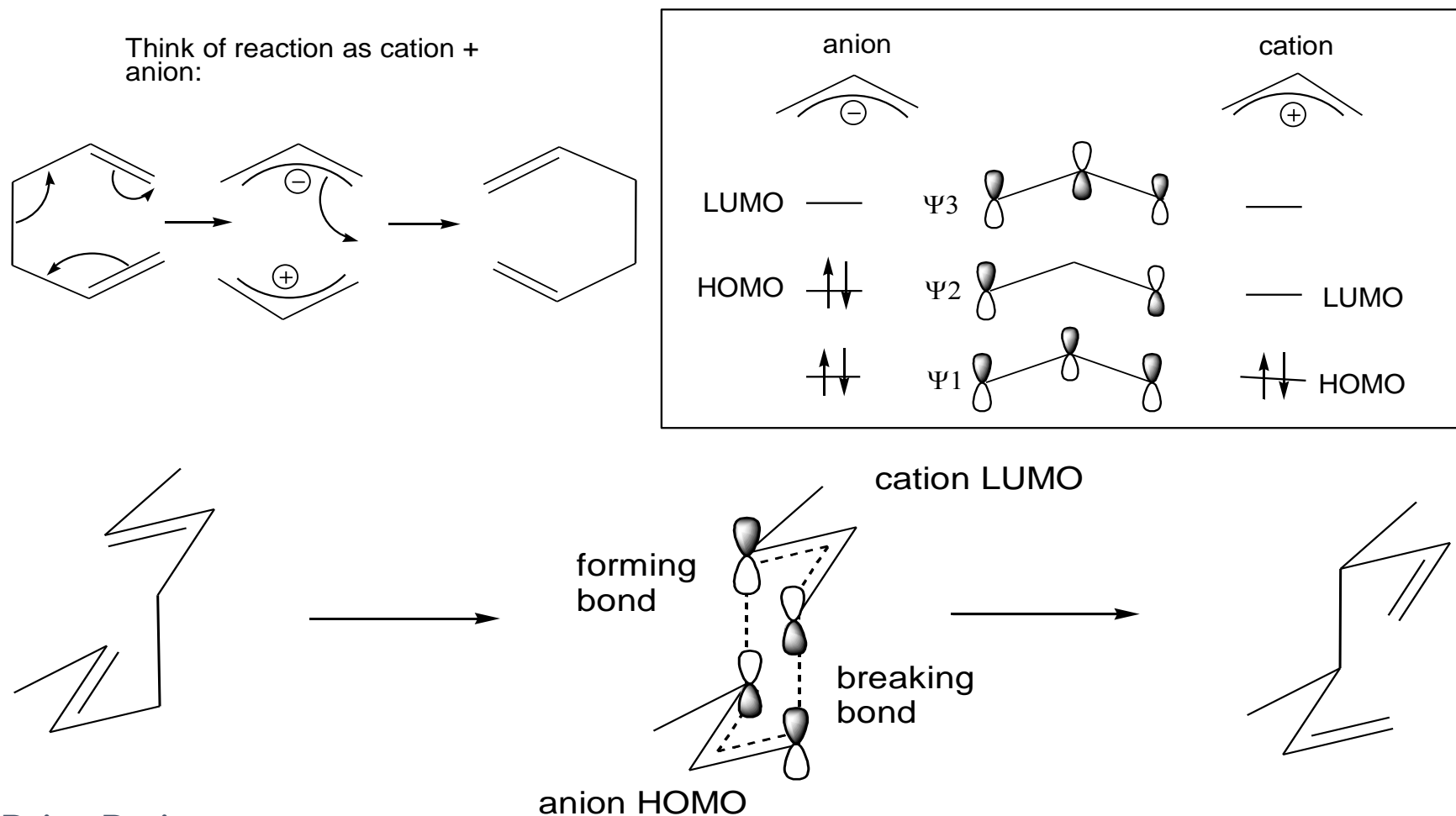
Cope Rearrangement



Oxy-Cope Rearrangement

Sigmatropic [3,3]-reactions proceed suprafacially:

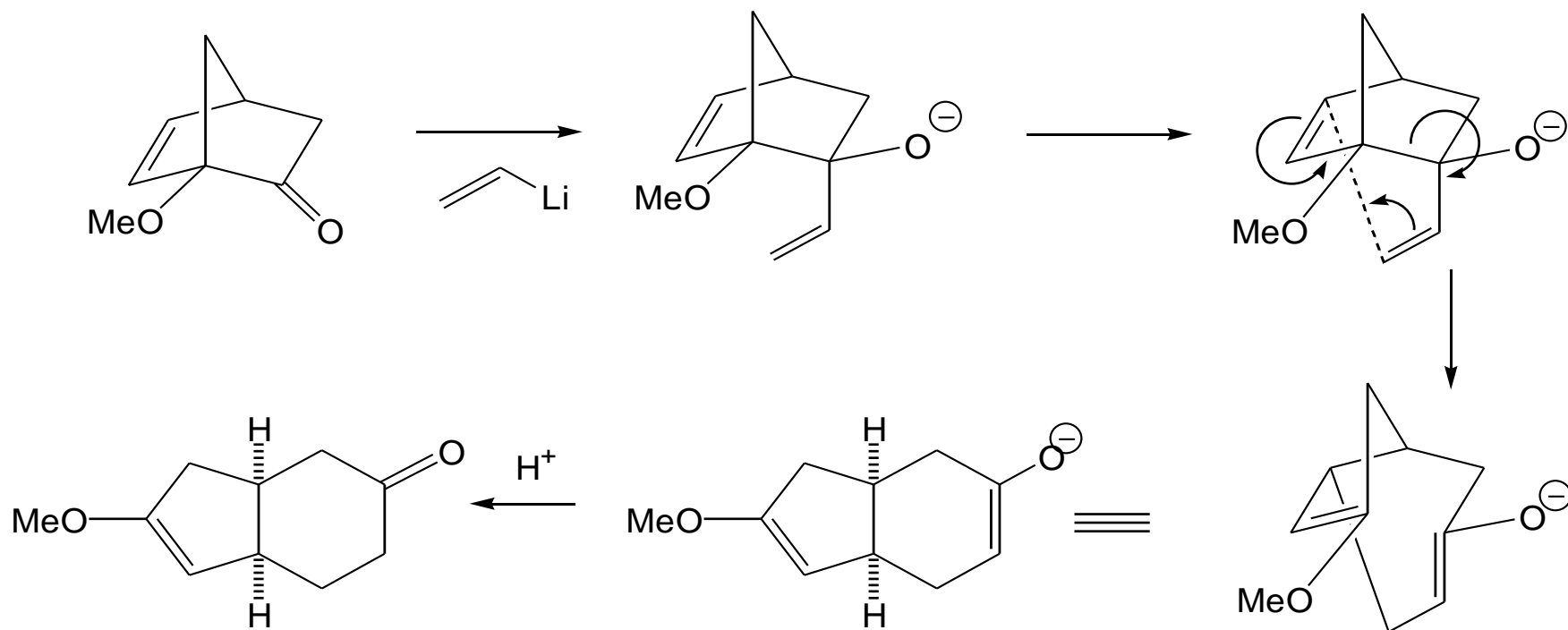
(4n+2) system hence Cope rearrangement is Suprafacial on each 3-carbon component according to orbital picture. Reactions proceed suprafacially via a chair-like transition state.



Cope Rearrangements : [3, 3] Sigmatropic Rearrangement

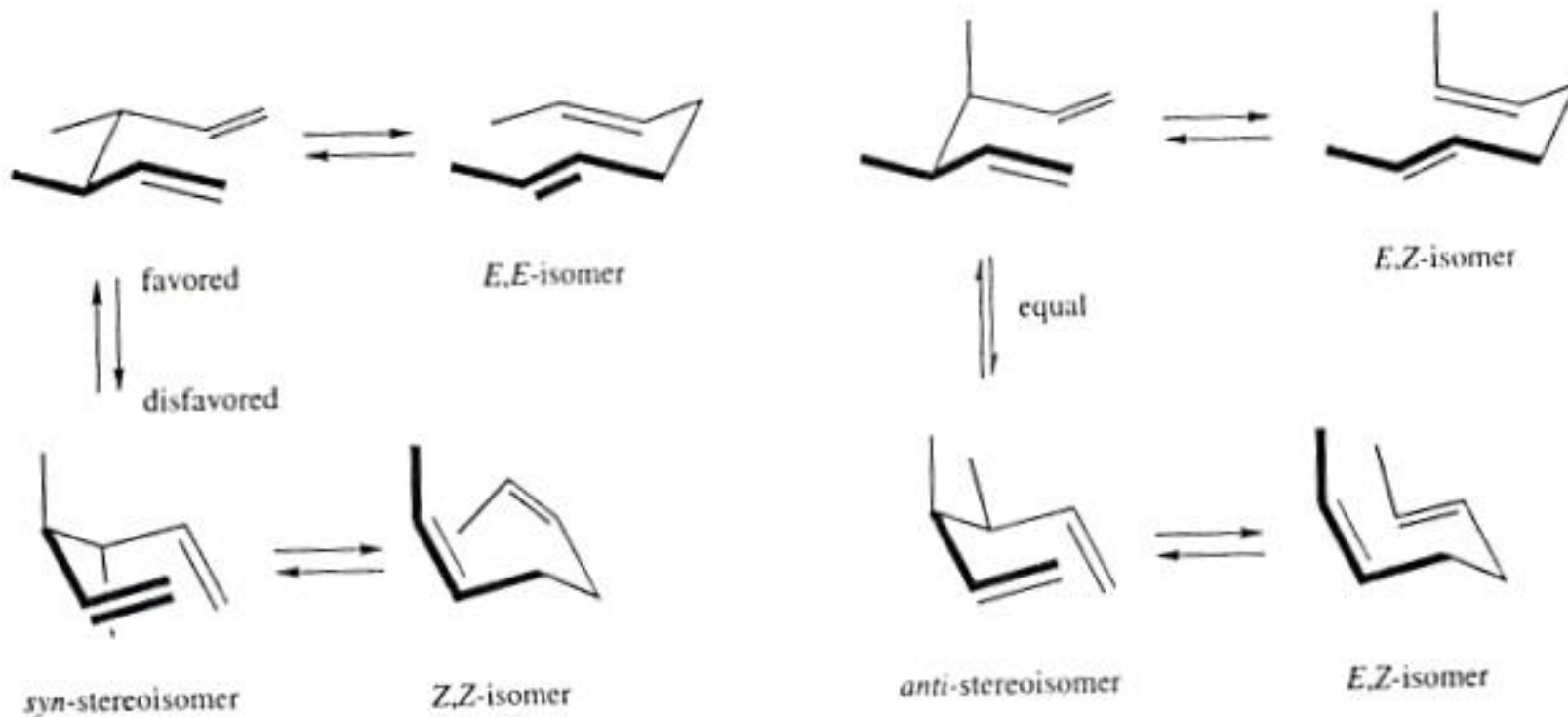
Applications and Examples

Cope rearrangements are often limited due to the reversibility of the reaction. However the reaction can be made irreversible by release of strain.



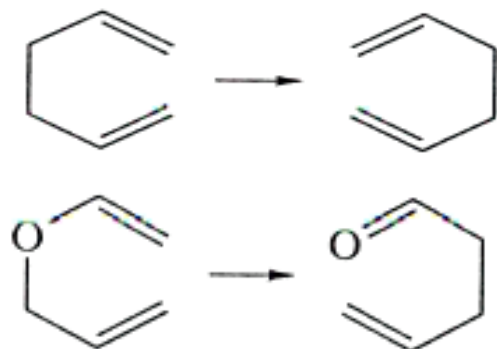
Cope Rearrangements : [3, 3] Sigmatropic Rearrangement

Reactions proceed suprafacially via a chair-like transition state and are of great synthetic utility:

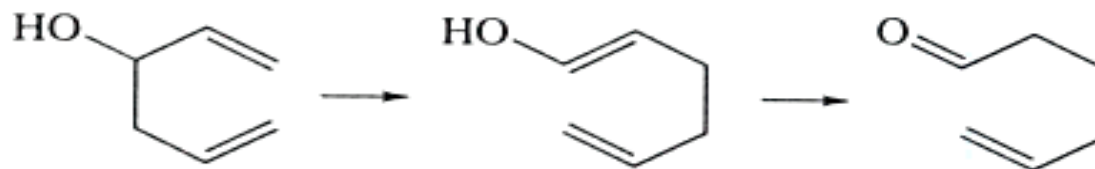


Cope and Oxy-Cope Rearrangements : Examples

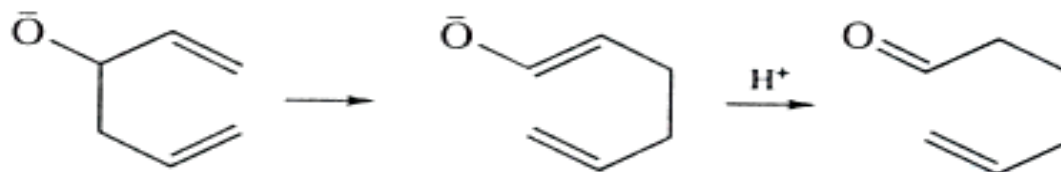
1^a Cope rearrangement



2^b Oxy-Cope rearrangement

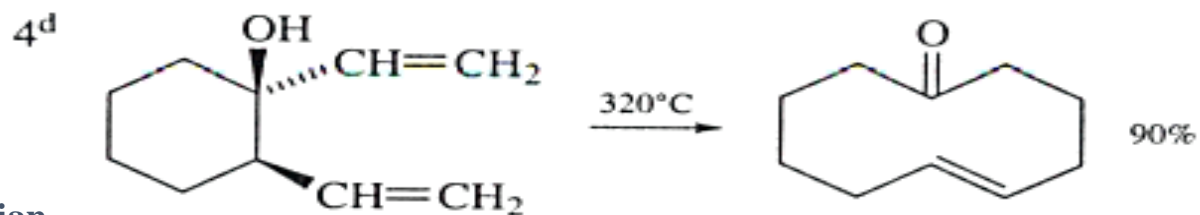
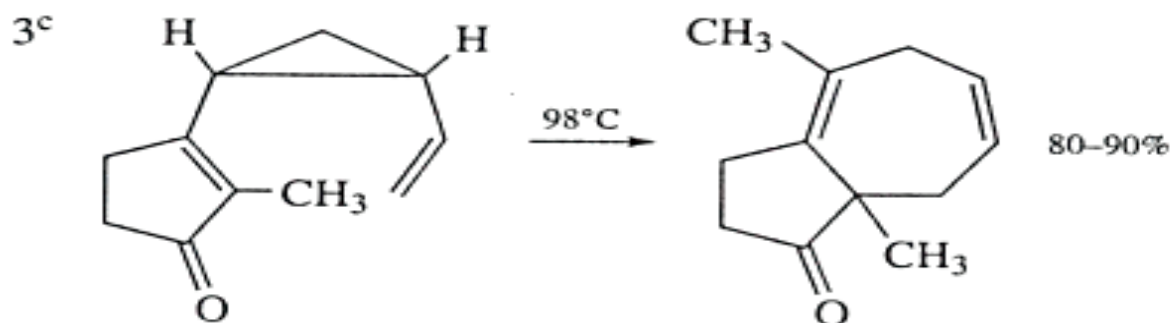
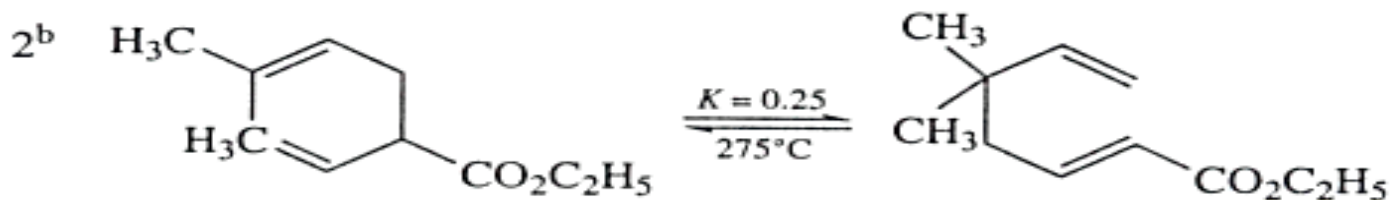
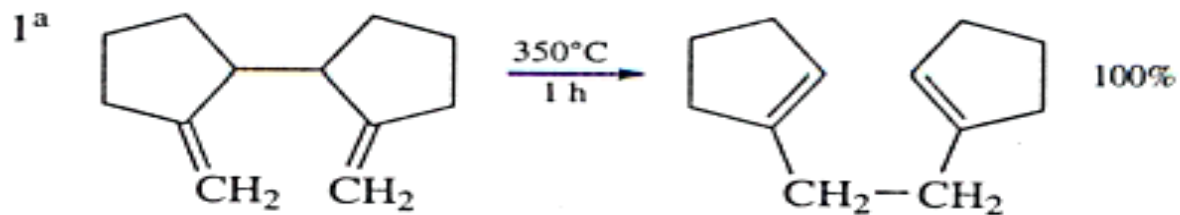


3^c Anionic oxy-Cope rearrangement

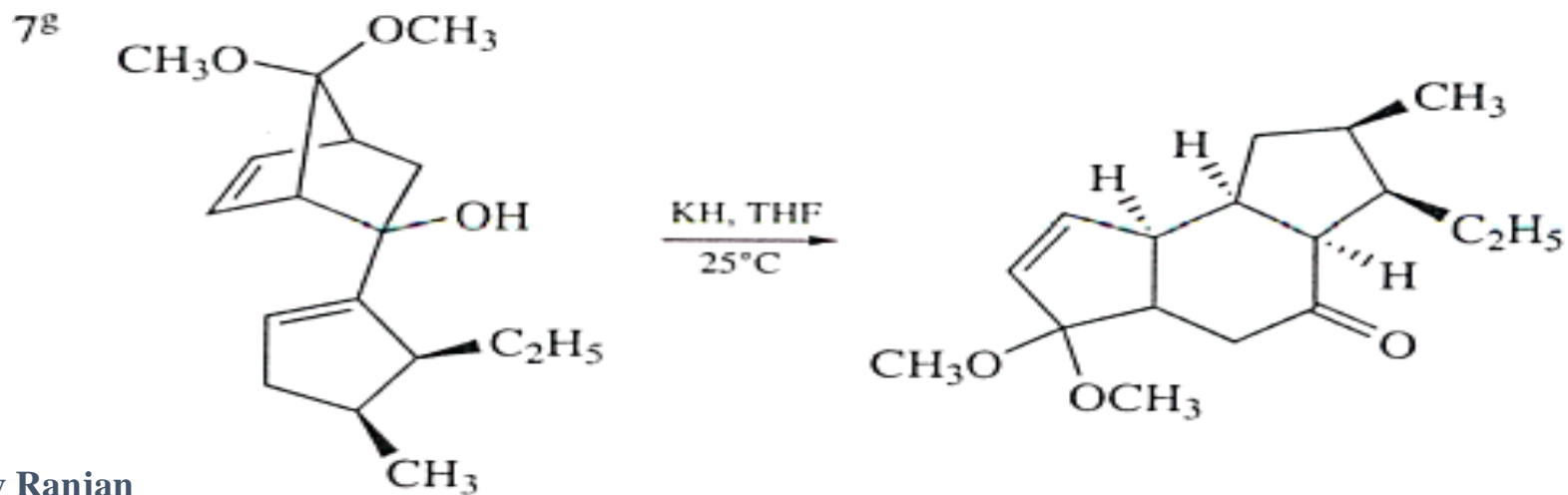
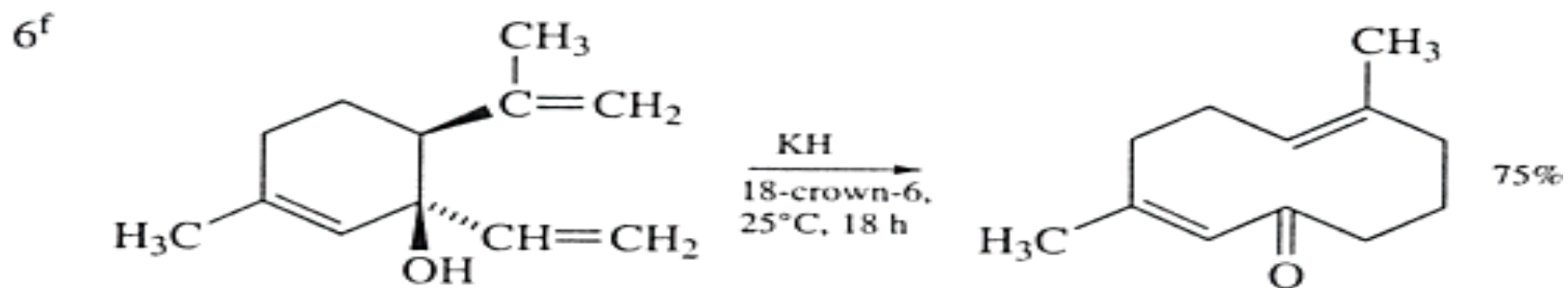


Cope Rearrangement : Examples

A. Thermal

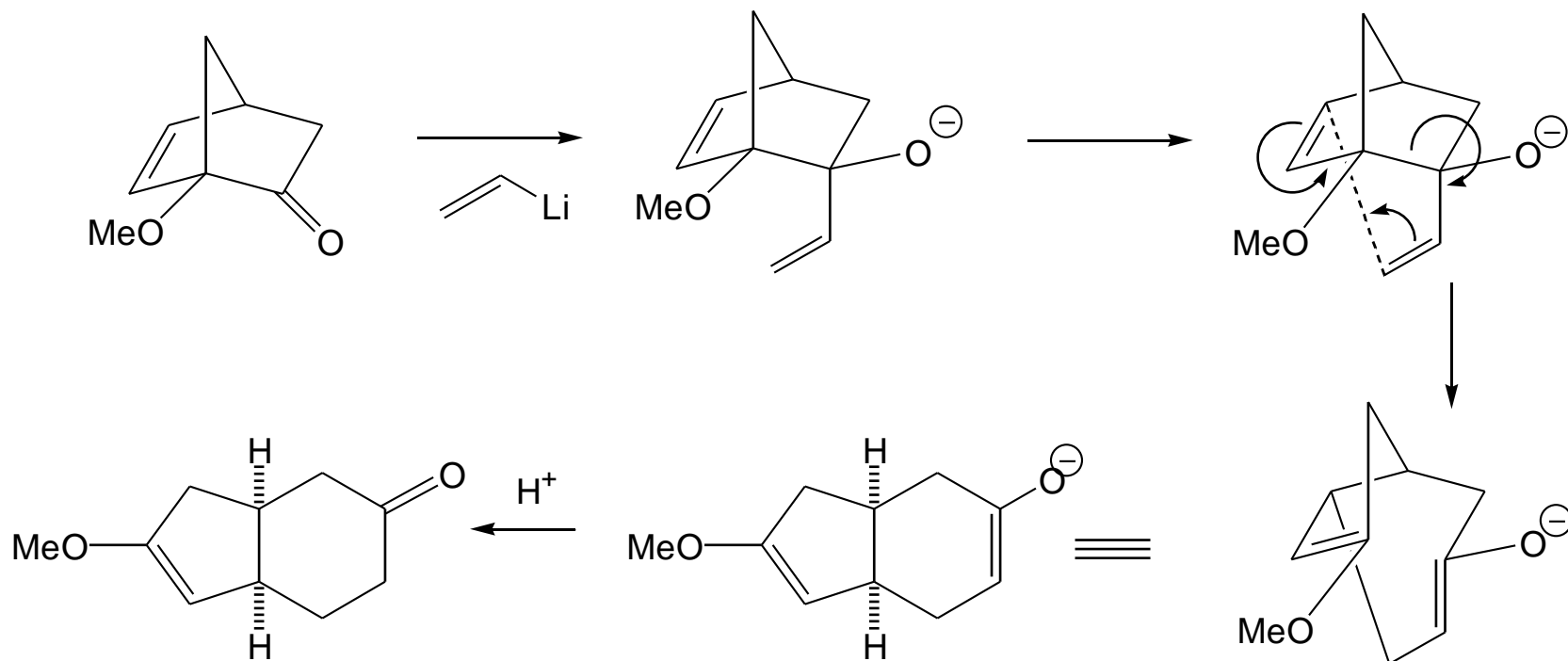


Oxy-Cope Rearrangement : [3, 3] Sigmatropic Rearrangement



COPE Rearrangement: Some More Applications

Cope rearrangements are often limited due to the reversibility of the reaction. However the reaction can be made irreversible by release of strain.



Thank You



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