

Sigmatropic reactions

These reactions are defined as involving migration of a σ bond that is flanked by one or more conjugated systems to a new position within the system

$$\begin{array}{c} \text{migrating } \sigma \text{ bond} \\ \hline \end{array}$$

The reaction is termed [i, j] sigmatropic shift when the bond migrates from position [1,1] to position [i,j].

$$\begin{array}{c} * \\ \\ R_1 \\ \\ R_2 \\ \\ R_1 \\ \\ R_2 \\ \end{array}$$

A Cope rearrangement

$$\begin{array}{c|c} C_6H_5 \\ \hline \Delta \\ \hline CH_3 \\ \end{array}$$

A Claisen rearrangement

Q. Give the product of the following reaction.

HO
$$\begin{array}{c}
\Delta \\
[3,3] \\
\text{IS},3]
\end{array}$$

$$\begin{array}{c}
\text{IS},3] \\
\text{IF}
\end{array}$$

$$\begin{array}{c}
\text{IS},3] \\
\text{IF}
\end{array}$$

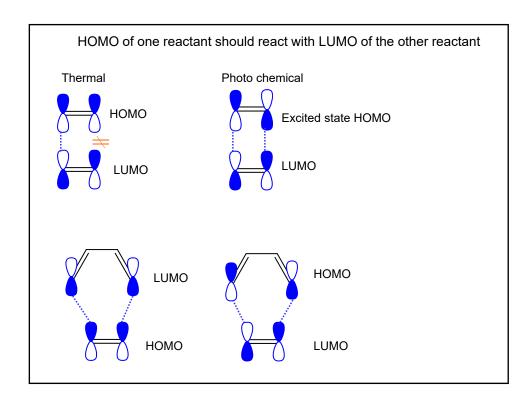
A biological reaction involving an electrocyclic reaction and a sigmatropic reaction

7-dehydrocholesterol, a steriod formed in skin, is converted into Vitamin \mathbf{D}_3 by two pericyclic reactions

- Deficiency in vitamin D causes rickets.
- Deficiency in vitamin D can be prevented by getting enough sun.
- Too much vitamin D is also harmful causes calcification of soft tissues skin pigmentation protects the skin from the sun's UV rays (it prevents the synthesis of too much vitamin D_3)

Cycloaddition reactions

• Why does maleic anhydride react easily with butadiene, but not at all with ethylene?



Q. Classify the following as [m+n] cycloaddition reactions

General description of Diels-Alder reaction

Dienes permanently in s-cis conformation undergo Diels-Alder reactions with ease

Dienes permanently in s-trans conformation cannot undergo Diels-Alder reaction

Q. Which of the following do not respond to the Diels-Alder reaction as a diene?

Ph

Q. Arrange the following dienes according to their reactivity towards Diels-Alder reaction

