Group Transfer Reaction

Another class of the pericyclic reaction is known **group transfer reaction**
where one or more groups of atoms is transferred from one molecule to another.

Group transfer reactions can sometimes be difficult to identify when separate reactant molecules combine into a single product molecule (like in the ene reaction).

Unlike other pericyclic reaction classes, group transfer reactions do not have a specific conversion of π-bonds into σ-bond or vice versa, and tend to be less frequently encountered.

Like all pericyclic reactions, group transfer reactions must obeys the Woodward–Hoffmann rules.

Group transfer reactions can be divided into two distinct subcategories:

i. the ene reaction and
ii. the diimide reduction.

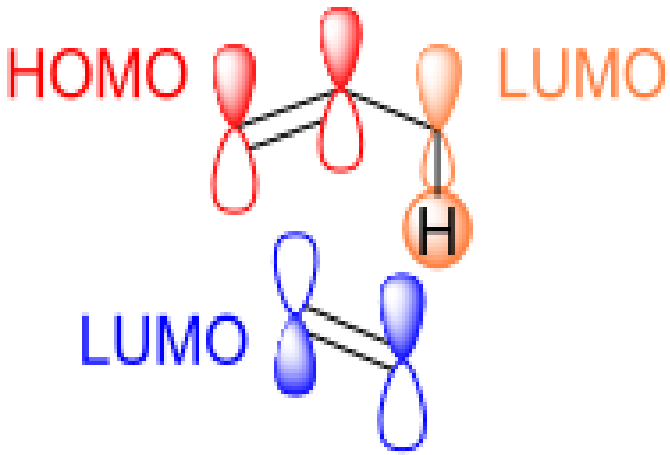
Group transfer reactions have diverse applications in various fields, including protein adenylation, biocatalytic and chemoenzymatic approaches for chemical synthesis, and strengthening skim natural rubber latex.

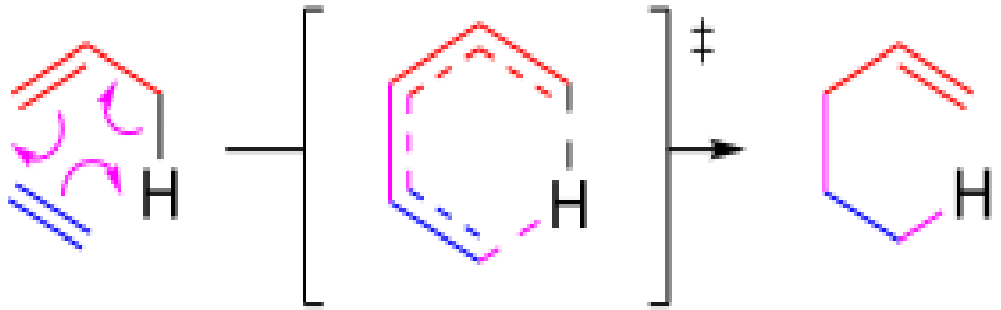
Mechanism

Defining feature of the group transfer reaction is that it is a concerted reaction, in which a bond is broken and formed in one step.

The concerted reaction occurs due to the orbital overlap between the alkene and the allylic enophile.

The electrons in the highest occupied molecular orbital (HOMO) of the ene are transferred to the lowest occupied molecular orbital (LUMO) of the enophile.





Mechanism of the group transfer reaction is allowed by the orbital overlap of the HOMO of the ene and the LUMO of the enophile.

Sub-classes of Group Transfer Reactions

The ene reaction

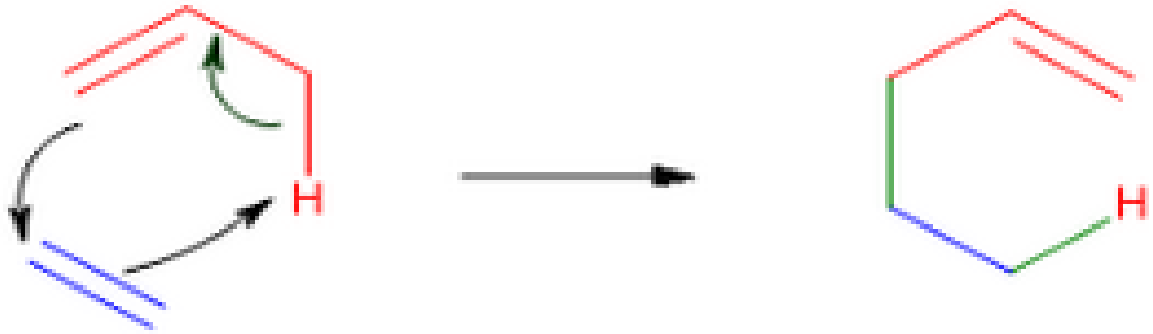
The ene reaction is one of the most common forms of group transfer reactions, where an allylic hydrogen is transferred to an alkene in a cyclic concerted mechanism.

The ene reaction reaction is further divided into subgroups including

i. intramolecular ene,
ii. metallo-ene, and
iii. carbonyl ene reactions.

The reverse reaction, commonly called the retro-ene reaction, can occur under high temperatures.

Ene: alkene, alkyne, allene, arene, C-heteroatom bond



Enophile: C=C, C=O, C=N, C=S, O=O, N=N, C≡C

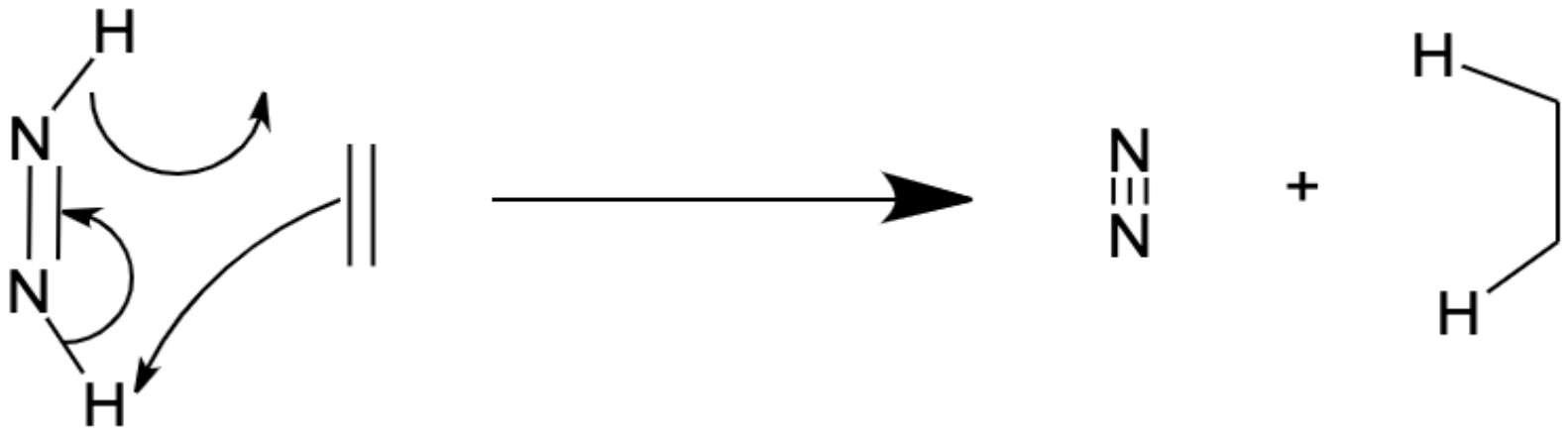
Generic ene reaction.

Reductions with diimide

Reductions with diimide is another class of group transfer reactions, in which alkenes and alkynes are reduced concertedly with diimide as the reducing agent.

In the generic mechanism of a reduction with diimide nitrogen gas is lost as a result. The diimide reduction displays a higher selectivity for the symmetrical homonuclear C=C double bond compared to the heteronuclear C=O double bond.

Along with a preference for reducing the least conjugated double bond, showcasing the precision of reductions with diimides in targeted organic synthesis.



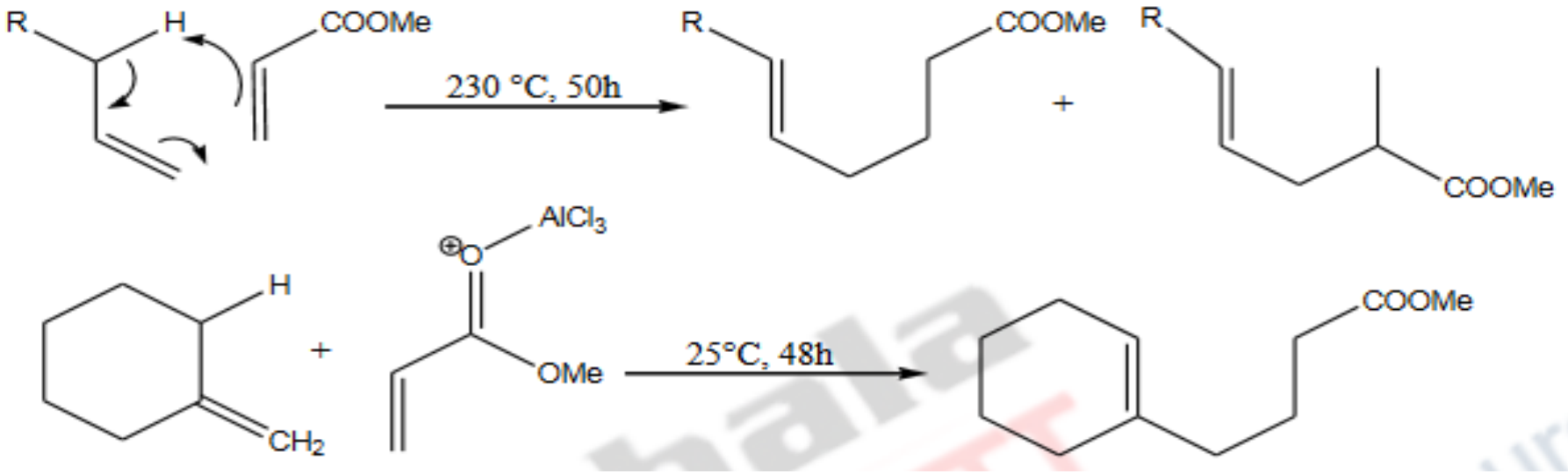
Generic mechanism of a reduction with diimide adapted from Mandal

Reaction between an alkene which has an allylic hydrogen known as the ene and a compound containing a multiple bond i.e the enophile is known as ene reaction which is also termed as Alder-ene Reaction.

They resemble [1, 5] sigmatropic rearrangement since a σ bond moves, and they also resemble cycloadditions like Diels-Alder reaction, with one of the π bond of the diene being replaced by a σ bond.

Nevertheless, since the reaction is bimolecular and no ring is formed, they are neither sigmatropic shifts nor cycloaddition reactions.

Following are examples of ene reactions.



Electron withdrawing groups on the enophile and electron donating groups on the ene favor the reaction.

Lewis acid catalyst such as $AlCl_3$ also lead to rate enhancement for ene reactions.

Woodward Hoffmann rules and Pericyclic reactions

Out of the four types of pericyclic reactions, three types of reactions can be distinguished by the number of σ bonds made or broken.

The following diagram gives a summary of number of bonds formed or broken.

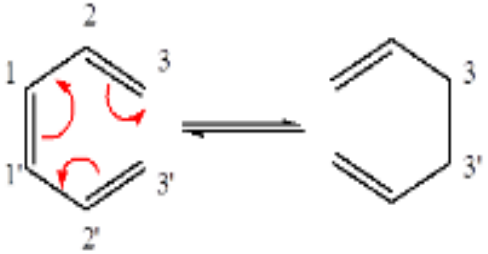
Types of pericyclic reaction

Cycloaddition reaction

Two new σ bonds are formed or broken

$\Delta\sigma = \pm 2$

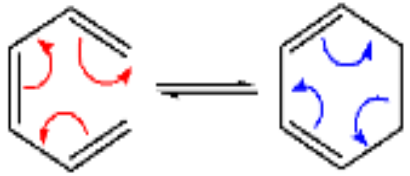
Sigmatropic rearrangement



One new σ bond is formed as another breaks

$\Delta\sigma = 0$

Electrocyclic reaction



One new σ bond is formed or broken

$\Delta\sigma = \pm 1$

Another unifying theme for pericyclic reaction is the Woodward-Hoffmann rules that govern feasibility and stereospecificity of pericyclic reactions.

Basee on Woodward-Hoffmann rules, reactions in which symmetry of molecular orbital (MO) is conserved involve a relatively low energy transition state and thus are symmetry allowed.

In contrast, reactions where symmetry of orbitals is destroyed by bringing one or more orbitals out of phase, the energy of transition state becomes too high because of antibonding interaction & therefore reaction becomes symmetry forbidden.

Another important rule is the fact that thermally allowed reactions are forbidden photochemically
and vice versa.

Also the products formed as a result of thermal tractions have opposite stereochemistry than products of a photochemical reaction.

Woodward-Hoffmann selection rules applied to various pericyclic reactions

	Thermal	Light
Electrocyclic reaction		
4n	Con	Dis
4n+2	Dis	Con
Cycloaddition reaction [p+q]		
4n	p_s+q_a or p_a+q_s	p_s+q_s or p_a+q_a
4n+2	p_s+q_s or p_a+q_a	p_s+q_a or p_a+q_s
Sigmatropic shift [i, j]		
4n	i_s+j_a or i_a+j_s	i_s+j_s or i_a+j_a
4n+2	i_s+j_s or i_a+j_a	i_s+j_a or i_a+j_s

a = antarafacial, s = suprafacia

References

https://en.wikipedia.org/wiki/Group_transfer_reaction

Singh, Jagdamba; Simha, Jaya (2005). Photochemistry And Pericyclic Reactions. New Age International. pp. 135–139. ISBN 9788122416947.

Hedberg, Christian; Itzen, Aymelt (2015-01-16). "Molecular Perspectives on Protein Adenylylation". ACS Chemical Biology. ***10*** *(1): 12–21. doi:10.1021/cb500854e. ISSN 1554-8929. PMID 25486069.*