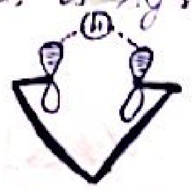
A (1,3) Supra shift of hydrogen is symmetry forbidden. Since the s orbital of hydrogen would have to overlap 'p' lobes of opposite face, hydrogen can not be bonded simultaneously to both carbons. A [1,5] Supra shift of hydrogen, on the other hand, is symmetry allowed.

[1,3] Shift
Symmetry forbidden



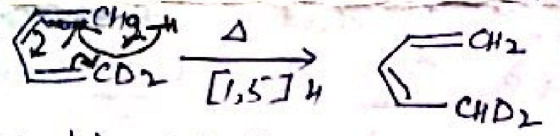
[1,5] Shift
Symmetry allowed

Suprafacial migration of hydrogen.

For larger π frame work, both supra and antara shifts should be possible on geometric grounds and stereochemistry will depend on orbital symmetry.

For photochemical reactions, predictions are reversed.

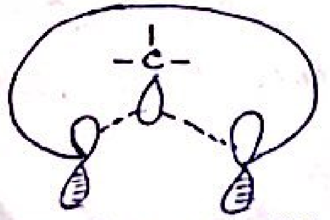
The facts also agree with above predictions. [1,3] Sigmatropic shifts of hydrogen are not known. however [1,5] shifts are well known.



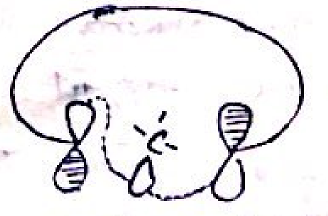
② Migration of Carbon

We have two possible kinds of bonding to the migrating group. one of them is similar to that of hydrogen i.e ① bonding of both ends of π framework to the same lobe of carbon: depending on the symmetry of π framework, the symmetry allowed migration may be suprafacial or antarafacial.

With carbon, a new concept of stereochemistry also appears. Bonding through the same lobe of carbon, means attachment to the same face of the atom i.e. retention of configuration in the migrating group.

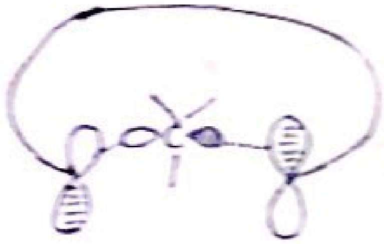


Suprafacial



Antarafacial

3. But there is second possibility for carbon i.e. bonding to the two ends of the π framework through different lobes of its p orbital. These lobes are on opposite faces of carbon like S_N2 reactions. Resulting inversion of configuration in the migrating group



Suprafacial

Antarafacial

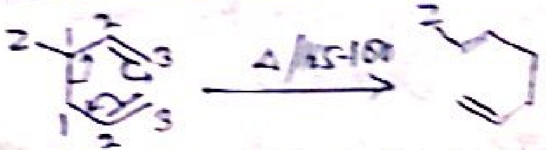
Inversion in group

For [1,3] and [1,5] shifts geometry prevents antarafacial migration. Thus it can be predicted that [1,3] migration occurs with inversion while [1,5] migration occurs with retention in configuration.

Thermal suprafacial migration of carbon have been found to occur with retention of configuration.

Simple Electrophilic nucleophilic and free radical 1,2 shifts may also be regarded as sigmatropic rearrangement.

① Cope-Rearrangement.



Z= Ph. RCO.

When hexa 1,5 dienes are heated, they isomerise in [3,3] sigmatropic rearrangement, known as Cope-Rearrangement.
When the diene is symmetrical, we get the product identical with the starting material.

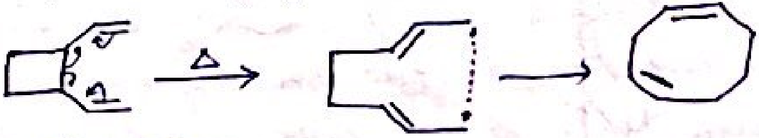
Therefore, a Cope-rearrangement can be detected only when the diene is not symmetrical about the bond. Any 1,5 diene will correspond to this rearrangement. The reaction occurs readily if there is any group at 3 or 4 the carbon, which can conjugate with any of the double bond.

The reaction is reversible, but can not be reversed with 3 hydroxy 1,5 diene because the product tautomerises to aldehydes or ketones. This reaction is known as Oxy-Cope-Rearrangement.

The reaction will not occurr if one of the double becomes part of an aromatic system

cis 1,2 divinyl cyclopropane undergoes rearrangement so rapidly that they can not be isolated at room temperature.

All cope rearrangement proceed with six membered cyclic intermediate. A diradical mechanism has been suggested for Cope rearrangement. A 1,6 bond is formed before 3,4 bond breaks so that a diradical mechanism is involved.

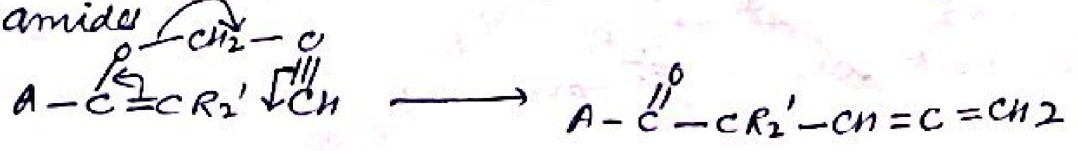


acta diene

1,2 divinyl
Cyclobutane

The rearrangement of $R_1CH=NR_2CHR_3(CH_2CH=CH_2)$ to $R_3CH=NR_2$ $CHR_1-CH_2-CH=CH_2$ has been called Aza-Cope-rearrangement

Propargyl, vinyl compounds give allenic aldehydes, ketones, esters or amides

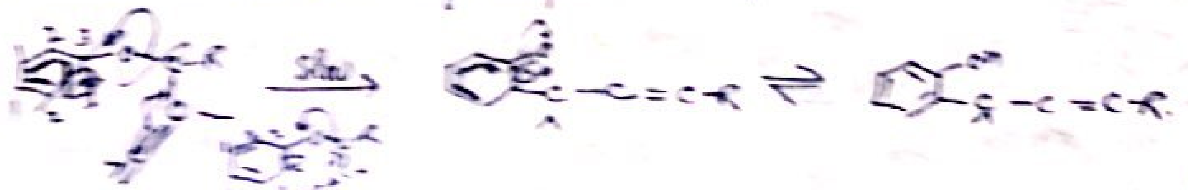


The conversion of Aryl-allyl thio ethers $ArSCH_2CH=CH_2$ to o-allyl-thiophenols is not possible because thiophenols are not stable and react to give bicyclic compounds. However many allyl vinyl ethers give this rearrangement.

② Claisen Rearrangement

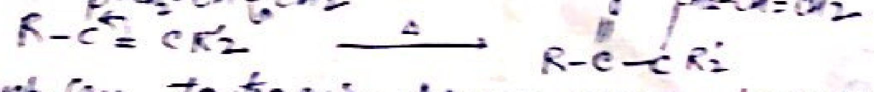
Aryl allyl ethers when heated rearrange to o-allyl phenols. This is known as Claisen Rearrangement

If both the ortho positions are filled, the allyl group migrates to para position. In ortho migration allyl group always undergoes allylic shift i.e. a substituent α to the oxygen now becomes γ to the ring. On the other hand there is no allylic shift in para migration. The allyl group is found exactly as it was in original ether. Mechanism is like [3,3] sigmatropic rearrangement and can be represented as



Propargyl groups (i.e. groups with triple bond) do not give the reaction. ~~Since the mechanism does not involve ions, it should not depend on presence or absence of substituent groups~~.

Electron donating groups increase rate of reaction, while electron attracting groups decrease it. Most Claisen rearrangement proceed without a catalyst. Solvent effects are greater. Rate varied over 300 fold range when the reaction was carried out in different solvents. CF_3CH_2OH has been found an exceptionally good solvent. Most commonly this rearrangement is performed without a catalyst but sometimes $AlCl_3$ and BF_3 have also been employed. In such case it resemble Friedel Crafts reaction, which no longer remain cyclic and ortho, meta and para products are formed. Allyl-vinyl ethers also undergo claisen rearrangement, infact the phenomenon was discovered with these compounds first.

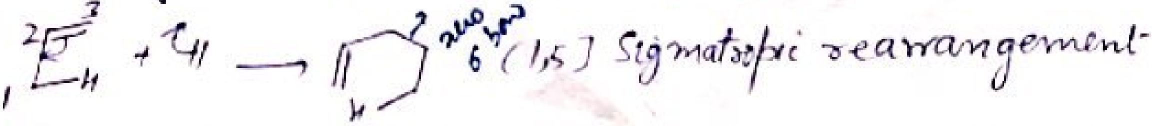


$$R-\overset{O-CH_2-CH=CH_2}{C}=CR'_2 \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-\overset{CH_2-CH=CH_2}{C}R'_2$$

In such case tautomerism does not occur because ketones are more stable than enols.

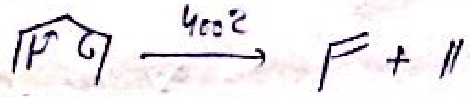
• Ene Reaction:

It involves the addition of an olefin having an allylic hydrogen, to a compound having a double bond (C=C, C≡C, N=N) with the formation of a new σ bond to the terminal carbon of the allyl group. This is followed by [1,5] migration of allylic hydrogen



In this reaction, activation energy is higher and so higher temp. is required than in Diel's - alder reaction. It is a concerted reaction involving a six membered transition state.

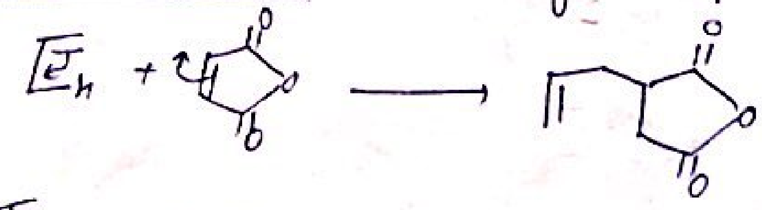
It is a reversible reaction and decomposition of 1-pentene at 400°c gives propylene and ethylene



Intra molecular ene reaction is also possible. 1,6 di'ene forms six membered ring product.

Synthetic Application: Following examples reveal ene reactions

①



②