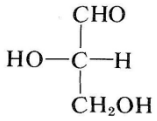
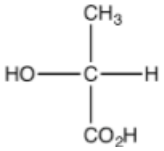
ORGANIC CHEMISTRY - II

UNIT – I **CODE : 18KP2CH05**

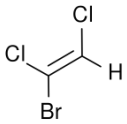
2 Marks

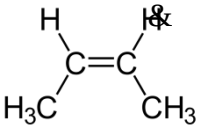
1. Define : Enatiomers
2. Meso tartaric acid is optically active give the reason?
3. Define : Chirality
4. What is plane of Symmetry? Give an example.
5. Write the condition of optical activity.
6. Define : Epimers.
7. Convert fisher projection of tartaric acid to sawhorse.
8. Write the configuration of the compounds.





9. What is racemic mixture?
10. Write the configuration of the compounds.





5 Marks

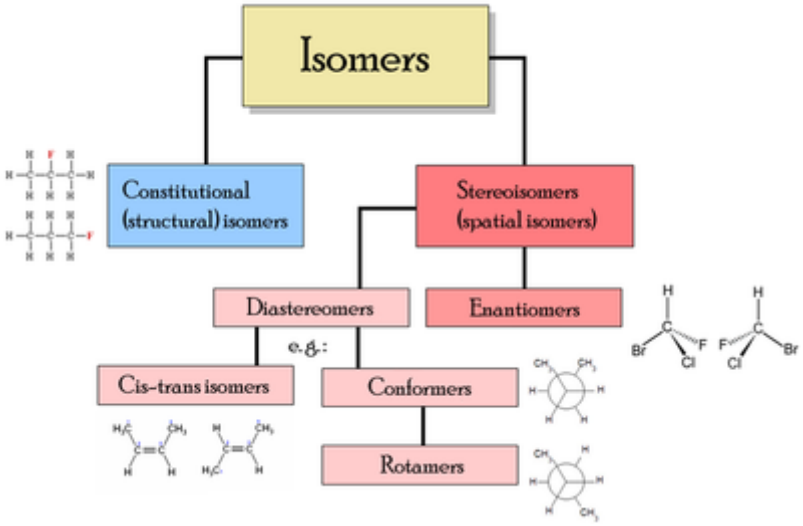
11. Explain the types of elements of symmetry.
12. Write the short notes on Newman projection.
13. Explain the interconversion of sawhorse projection of 2,3 dibromobutane to fisher projection via newman projection.
14. Discuss the optical rotation theory.
15. Write the conditions for absolute configuration.

10 Marks

16. Explain briefly about Biphenyls and allenes
17. Write short notes on (i) Fisher Projection (ii) Sawhorse Projection
18. Discuss the nomenclature of E/Z isomer with different examples.
19. Discuss the optical activity of erythrose.

STEREOCHEMISTRY

Stereochemistry is the study of how molecules are affected by the way their atoms are arranged in space. It is also known as 3D chemistry as the word *stereo* means *three dimensional*. Using stereochemistry, chemists can work out the relationships between different molecules that are made up from the same atoms. They can also study the effect on the physical or biological properties these relationships give molecules. When these relationships influence the reactivity of the molecules it is called dynamic stereochemistry.



The different types of isomers. Stereochemistry is the study of stereoisomers

In chemistry, some molecules have more than one isomer. This means that molecules can have different forms, even though all the forms made up of the same atoms. There are two kinds of isonomers. Constitutional isomers have the same atoms, but they are joined differently. Stereoisomers have the same atoms, they are joined the same way, but the atoms are arranged differently in space. An important part of stereochemistry is the study of chiral molecules. These molecules look almost identical, except that one molecule is the mirror image of the other.

In most chemical bonds, the atoms of a molecule free to move around without breaking the bonds. When a molecule has a double bond or a ring structure, the molecule can be sorted into different isomers. These are molecules with the same chemical structure but different forms.

Principles of Symmetry

Axis of Symmetry

An axis around which a rotation by results in a molecule indistinguishable from the original. This is also called an *n*-fold rotational axis and abbreviated C_n. Examples are the C_2 axis in water and the C_3 axis in ammonia. A molecule can have more than one symmetry axis; the one with the highest *n* is called the principal axis, and by convention is aligned with the z-axis in a Cartesian coordinate system.

Plane of symmetry:

A plane of reflection through which an identical copy of the original molecule is generated. This is also called a mirror plane and abbreviated σ (sigma = Greek "s", from the German 'Spiegel' meaning mirror). Water has two of them: one in the plane of the molecule itself and one perpendicular to it. A symmetry plane parallel with the principal axis is dubbed *vertical* (σ_v) and one perpendicular to it *horizontal* (σ_h). A third type of symmetry plane exists: If a vertical symmetry plane additionally bisects the angle between two 2-fold rotation axes perpendicular to the principal axis, the plane is dubbed dihedral (σ_d). A symmetry plane can also be identified by its Cartesian orientation, e.g., (xz) or (yz).

Centre of symmetry or **inversion centre** (i)

A molecule has a centre of symmetry when, for any atom in the molecule, an identical atom exists diametrically opposite this centre an equal distance from it. In other words, a molecule has a centre of symmetry when the points (x,y,z) and (−x,−y,−z) correspond to identical objects. For example, if there is an oxygen atom in some point (x,y,z), then there is an oxygen atom in the point (−x,−y,−z). There may or may not be an atom at the inversion centre itself. Examples are xenon tetrafluoride where the inversion center is at the Xe atom, and benzene (C_6H_6) where the inversion centre is at the centre of the ring.

Newman projection

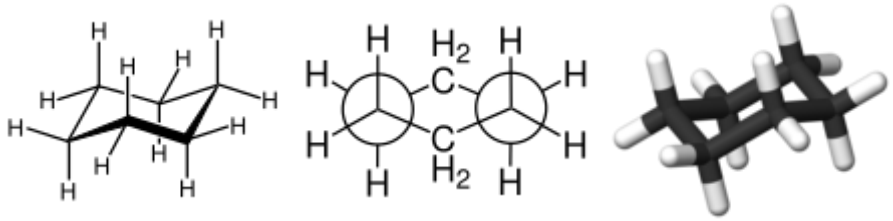
A Newman projection, useful in alkane stereochemistry, visualizes the conformation of a chemical bond from front to back, with the front atom represented by a dot and the back carbon as a circle. The front carbon atom is called *proximal*, while the back atom is called *distal*. This type of representation clearly illustrates the specific dihedral angle between the proximal and distal atoms.

This diagram style is an alternative to a sawhorse projection, which views a carbon-carbon bond from an oblique angle, or a wedge-and-dash style, such as a Natta projection.

These other styles can indicate the bonding and stereochemistry, but not as much conformational detail.

This projection is named after American chemist Melvin Spencer Newman, who introduced it in 1952 as partial replacement for Fischer projections, which are unable to represent conformations and thus conformers properly.

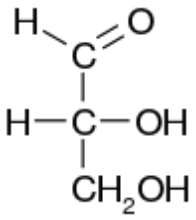
A Newman projection can be used to visualize any sort of bond, not just a single bond between carbons of an alkane. For example, it can be used to study cyclic molecules, such as the chair conformation of cyclohexane:



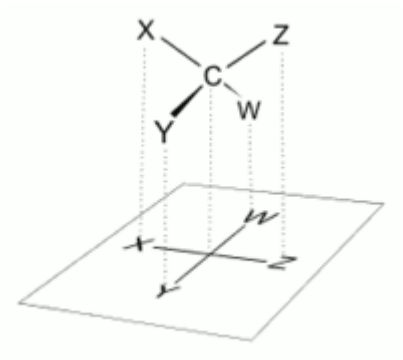
Bond-line structure Newman projection 3D structure

Fischer projection

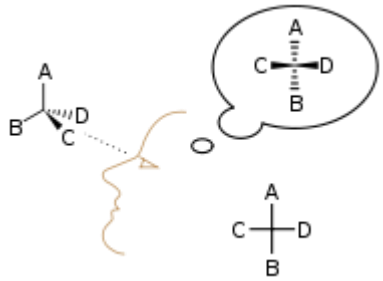
The Fischer projection, devised by Emil Fischer in 1891, is a two-dimensional representation of a three-dimensional organic molecule by projection. Fischer projections were originally proposed for the depiction of carbohydrates and used by chemists, particularly in organic chemistry and biochemistry. The use of Fischer projections in non-carbohydrates is discouraged, as such drawings are ambiguous when confused with other types of drawing.



Fischer projection of D-Glyceraldehyde



Projection of a tetrahedral molecule onto a planar surface.

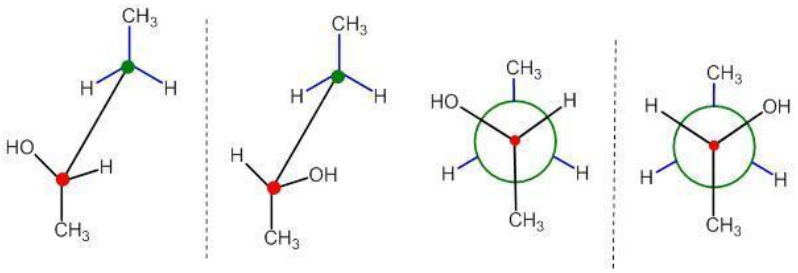


Visualizing a Fischer projection.

Sawhorse projection

A sawhorse projection is similar to a Newman projection, but it shows the carbon-carbon bond that is hidden in a Newman projection. Just as with Newman projections, you can draw sawhorse projections in eclipsed and staggered conformations. Below is a sawhorse projection of the gauche conformation of butane. They are called sawhorse projections because the eclipsed conformation looks like a carpenter's sawhorse. Sawhorse projections are useful for determining if two molecules are enantiomers or diastereomers. They make it easier to see if the structures are mirror images or superimposable.

Here are the sawhorse and Newman projections of butan-2-ol.



Sawhorse and Newman representations for the 2 enantiomers of 2-Butanol

Interconversion of Projection Formula

It is important to have a clear idea of the inter-relationship between various projections of a given organic molecule to understand the stereochemical implications of the reactions. For this, we should be well conversant with the methods of translating one projection into another. The methods used for the interconversion of one projection formula into another form without changing the configuration are given in the following description.

Interconversion of Fischer Projection Formula into Sawhorse Projection and vice-versa

(i) Fischer Projection to Sawhorse Projection

Fischer projection of a compound can be converted into Sawhorse projection; first in the eclipsed form (in Fischer projection the groups on neighbouring carbons are considered to be eclipsing each other), by holding the model in horizontal plane in such a way that the groups on the vertical line point above, and the last numbered chiral carbon faces the viewer. Then, one of the two carbons is rotated by an angle of 180^0 to get the staggered form (more stable or relaxed form).

For example, Fischer projection of an optically active tartaric acid is converted into staggered Sawhorse projection as shown.

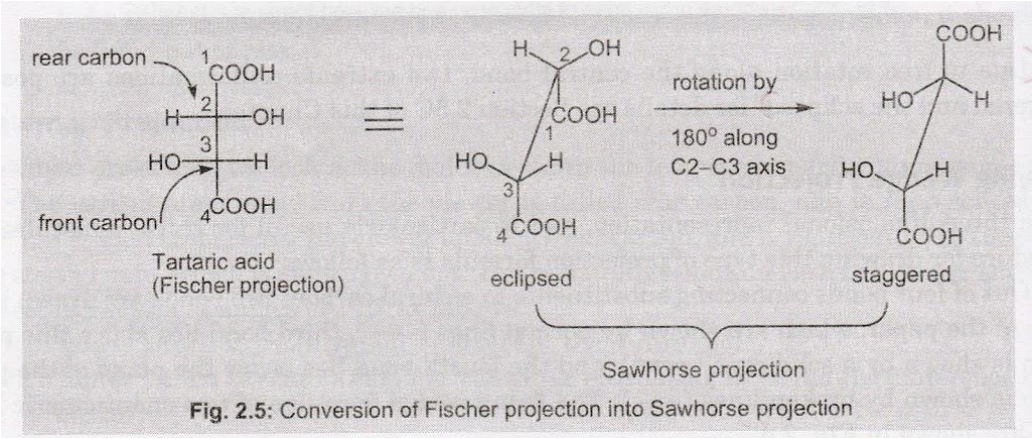


Fig. 2.5: Conversion of Fischer projection into Sawhorse projection

(ii) Sawhorse Projection to Fischer Projection

First, the staggered Sawhorse projection is converted to an eclipsed projection. It is then held in the vertical plane in such a manner that the two groups pointing upwards are away from the viewer, i.e. both these groups are shown on the vertical line. Such a conversion for 2,3-dibromobutane is shown.

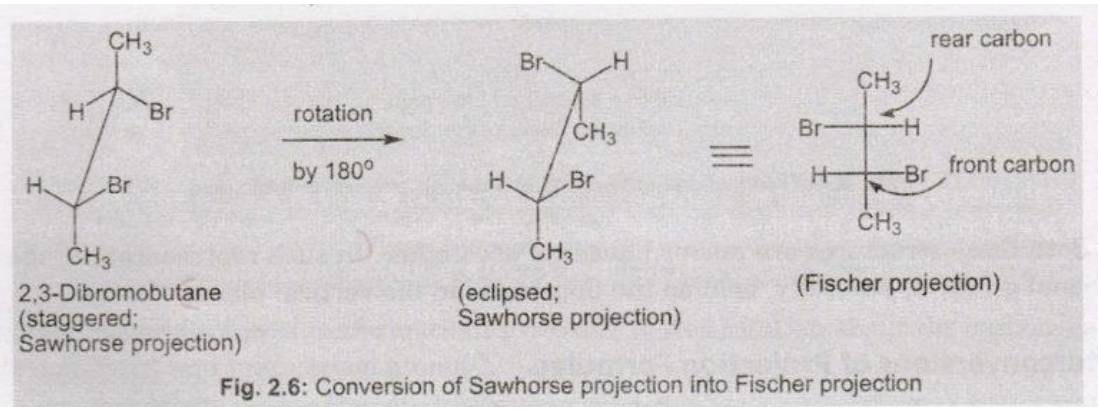


Fig. 2.6: Conversion of Sawhorse projection into Fischer projection

Interconversion of Sawhorse Projection Formula to Fischer Projection via Newman Projection and vice-versa

(i) Sawhorse Projection to Newman Projection And then Fischer Projection

Conversion of Sawhorse projection to Newman projection is quite easy. The molecule is viewed from front carbon (the central C-C bond being invisible) to get the staggered Newman projection. The rear carbon is rotated by 180° to get eclipsed Newman projection. Then, the

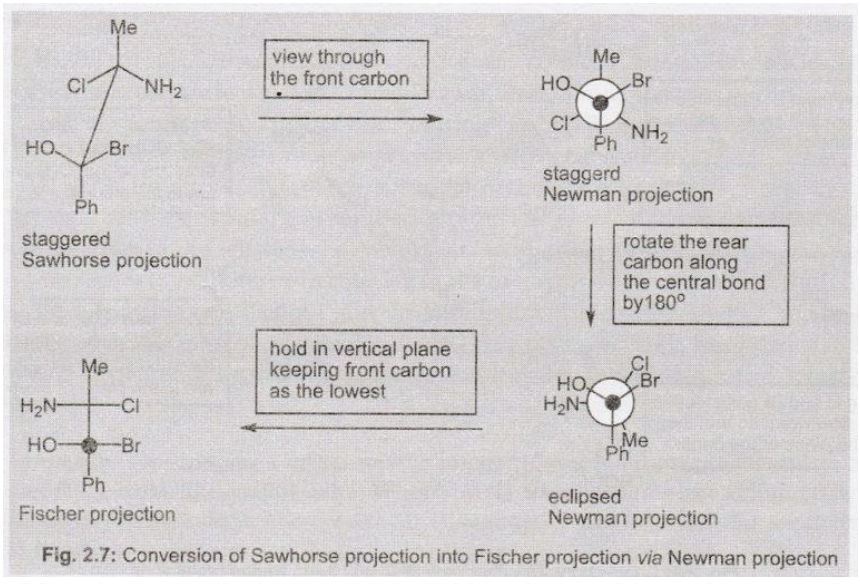


Fig. 2.7: Conversion of Sawhorse projection into Fischer projection *via* Newman projection

molecule is held in the vertical plane, i.e. central bond is visible in the vertical plane in such a manner that front carbon is the lowest carbon.

(ii) Fischer Projection to Newman Projection and then Sawhorse Projection:

The molecule is viewed through the lowest chiral carbon, which becomes the front carbon, and thus eclipsed Newman projection is drawn. It is then converted into staggered

conformation. Finally, the molecule is viewed through the bond connecting the front carbon with rear carbon. Such a conversion of D-erythrose is illustrated in the following scheme.

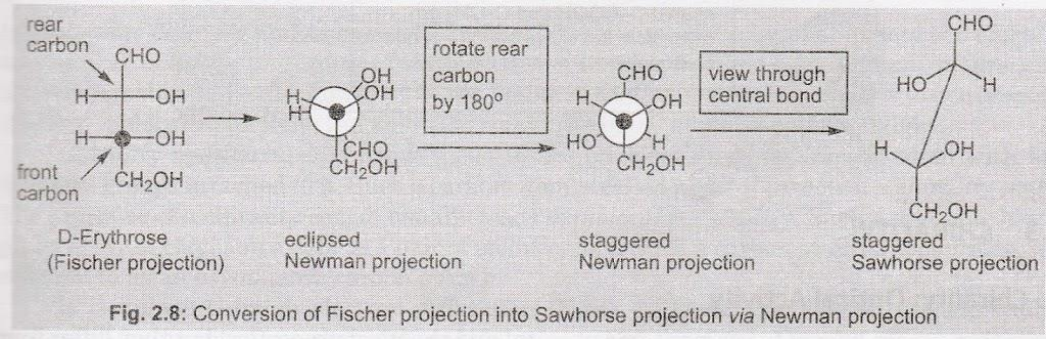


Fig. 2.8: Conversion of Fischer projection into Sawhorse projection *via* Newman projection

Interconversion of Fischer Projection Formula into Flying Wedge Projection and vice-versa

In this topic, we will be discussing the Interconversions of Fischer Projection Formula into Flying Wedge Projection form. Then we will be talking the conversion of Flying Wedge Projection into Fischer form.

(i) Fischer Projection to Flying Wedge Projection

The vertical bonds in the Fischer projection are drawn in the plane of the paper using simple lines(—). Consequently, horizontal bonds will project above and below the plane (‘a’ and ‘b’ in the fig.). Conversion of Fischer projection of one of the enantiomers of α-bromopropanoic acid into five flying wedge formulae (without changing the configuration) is illustrated in the fig.

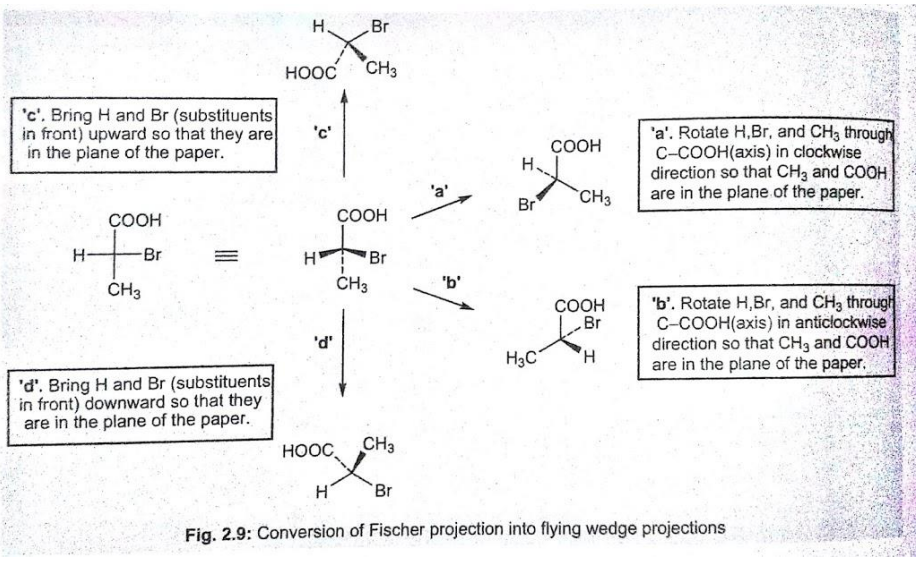
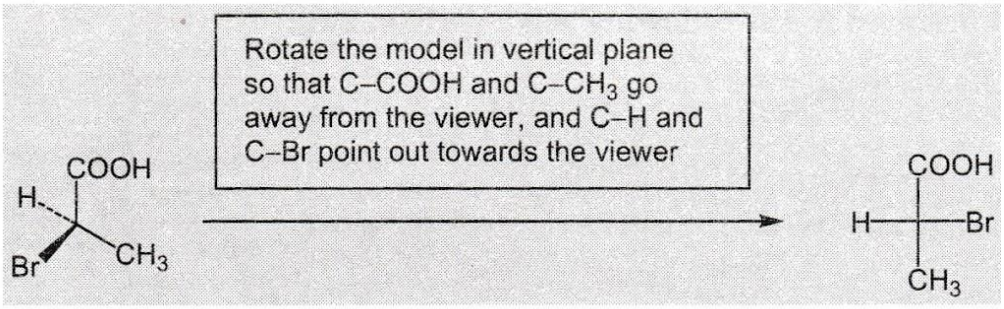


Fig. 2.9: Conversion of Fischer projection into flying wedge projections

(ii) Flying Wedge Projection to Fischer Projection:

The molecule is rotated (in the vertical plane) in such a way that the bonds shown in the plane of the paper go away from the viewer, and are vertical.



Stereoisomers are properly named using the Cahn-Ingold-Prelog (CIP) priority rules to decide which parts of the molecule to consider first.

The rules have evolved to cover many situations, but the basic rules are:

1. Consider the first atom of each part of the molecule. An atom with higher atomic number has higher priority. (e.g. I > Cl > C > H)
2. If the first atom of two groups is the same, consider the second atom(s) in the same way as the first. (e.g. $-C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3 > -CH_3$). If this does not assign priority, consider the next atoms until there is a difference.

Realize that when you do this it will mean that sometimes groups with higher total weights will have lower priority because of a lower weight of the atom that connects them.

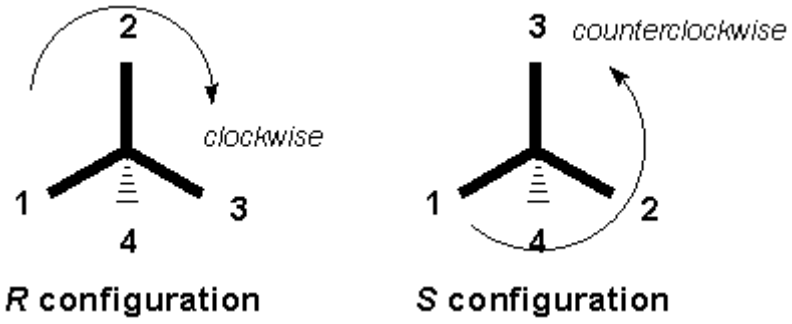
R- and S-notation

R- and S-notation use the CIP priority rules for the assignment of the *absolute configuration* around a stereocenter.

First, assign priorities as described above to each bonded group surrounding the stereocenter (1, highest to 4, lowest).

Second, point the lowest priority (4) atom away from you. Follow the direction of the remaining 3 priorities from highest to lowest priority (lowest to highest number, 1<2<3).

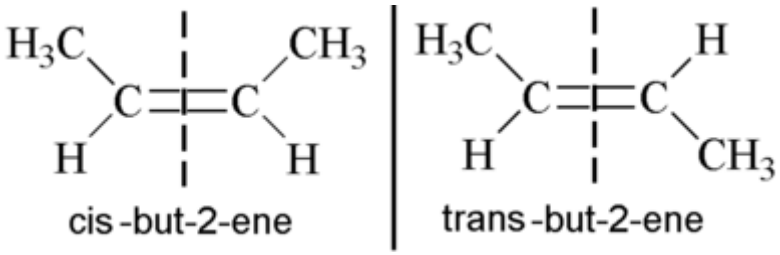
A counterclockwise direction is an S (*sinister*, Latin for left) configuration. A clockwise direction is an R (*rectus*, Latin for right) configuration.



1. According to the atomic number when only atom is present and in a group the direct attached atom is considered with atomic number.
2. When two or more groups have similar first atom, the priority is determined by considering the atomic number of second atom.
3. If the first atom of two same groups have same substitutes of higher no will get more priority.
4. More atomic number containing atom and how many atoms are present of the higher atomic number containing elements.

E/Z Notation

Earlier in stereochemistry, we discussed cis/trans notation where cis- means same side and trans- means opposite side. Alkenes can present a unique problem, however in that the cis/trans notation sometimes breaks down. The first thing to keep in mind is that alkenes are planar and there's no rotation of the bonds, as we'll discuss later. So when a substituent is on one side of the double-bond, it stays on that side.



cis-but-2-ene and trans-but-2-ene

The above example is pretty straight-forward. On the left, we have two methyl groups on the same side, so it's cis-but-2-ene. And on the right, we have them on opposite sides, so we have trans-but-2-ene. So in this situation, the cis/trans notation works and, in fact, these are the correct names.

(E)-3-methylpent-2-ene and (Z)-3-methylpent-2-ene

From the example above, how would you use cis and trans? Which is the same side and which is the opposite side? Whenever an alkene has 3 or 4 differing substituents, one must use the what's called the EZ nomenclature, coming from the German words, Entgegen (opposite) and Zusammen (same).

Let's begin with (Z)-3-methylpent-2-ene. We begin by dividing our alkene into left and right halves. On each side, we assign a substituent as being either a high priority or low priority substituent. The priority is based on the atomic number of the substituents. So on the left side, hydrogen is the lowest priority because its atomic number is 1 and carbon is higher because its atomic number is 6.

On the right side, we have carbon substituents on both the top and bottom, so we go out to the next bond. On to the top, there's another carbon, but on the bottom, a hydrogen. So the top gets high priority and the bottom gets low priority.

Because the high priorities from both sides are on the same side, they are Zusammen (as a mnemonic, think 'Zame Zide').

Now let's look at (E)-3-methylpent-2-ene. On the left, we have the same substituents on the same sides, so the priorities are the same as in the Zusammen version. However, the substituents are reversed on the right side with the high priority substituent on the bottom and the low priority substituent on the top. Because the High and Low priorities are opposite on the left and right, these are Entgegen, or opposite.

The system takes a little getting used to and it's usually easier to name an alkene than it is to write one out given its name. But with a little practice, you'll find that it's quite easy.

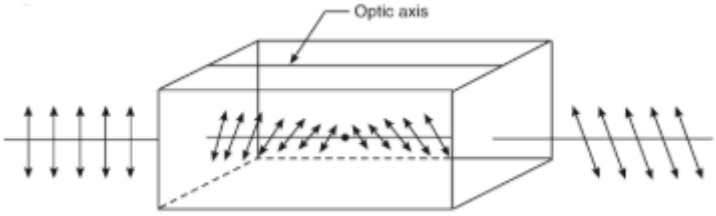
Optical Rotation

The optical rotation is the angle through which the plane of polarization is rotated when polarized light passes through a layer of liquid.
Optical activity is the ability of a compound to rotate the plane of polarized light. This property arises from an interaction of the electromagnetic radiation of polarized light with the unsymmetric electric fields generated by the electrons in a chiral molecule.

A compound is said to be optically active when the linearly polarized light is being rotated when it is passing through it. The optical rotation is the angle through which the plane of polarization is rotated when polarized light passes through a layer of a liquid. Optical rotation is the effect which is determined by the concentration of chiral molecules and their molecular structure in a substance. Every optical active substance has its own specific rotation.

Optical Rotation Theory

The optical rotation that is the rotation of the plane of polarized light is shown below.



Optical Rotation

The ability to rotate the plane of polarization of plane-polarized light by a certain substance is called optical activity. Substances that have the ability to rotate the plane of the polarized light passing through them are called optically active substances. Quartz and cinnabar are examples of optically active crystals while aqueous solutions of sugar, tartaric acid are optically active solutions.

Optically active substances are classified into two types.

1. **Dextrorotatory substances –** Substances that rotate the plane of polarization of the light towards the right are known as right-handed or dextrorotatory.
2. **Laevorotatory substances –** Substances which rotate the plane of polarization of the light toward the left are known as left-handed or **Laevorotatory.**

Optical isomerism

Optical isomerism is a case where the isomers display identical characteristics in terms of molecular weight as well as chemical and physical properties. However, they differ in their effect on the rotation of polarized light.

Optical isomerism occurs mainly in substances that have the same molecular and structural formula, but they cannot be superimposed on each other. In simple words, we can

say that they are mirror images of each other. Alternatively, it can also be found in substances that have an asymmetric carbon atom.

Typically, optical isomerism is shown by stereoisomers which rotate the plane of polarized light. If the plane of polarized light passing through enantiomer solution rotates in the clockwise direction then the enantiomer is said to exist as (+) form and if the plane of polarized light rotates in anti-clockwise direction then the enantiomer is said to exist in (-).

For example, an enantiomer of alanine (amino acid) which rotates the plane of polarized light in clockwise and anti-clockwise direction can be written as (+) alanine and. (-) alanine respectively.

The extent of rotation of plane-polarized light by the two enantiomeric form is exactly the same but the direction of rotation is opposite. Moreover, if the two enantiomer pair are present in equal amount then the resultant mixture is called a racemic mixture. This means that 50% of the mixture exists in (+) form and the other 50% exist in (-) form.

Since racemic mixture rotates the plane of polarized light equally in the opposite direction, the net rotation is zero. Therefore racemic mixture is optically inactive.

Origin of Optical Isomers

To determine whether the compound is optically active or not, we have to first see whether the carbon is attached to four different groups or not. For a better understanding of optical isomerism, let us take an example of two models of organic compound as shown below;

These two models have the same bonding arrangement of the atom but a different spatial arrangement. From the above model of A and B, it is clear that the arrangement of the blue and orange group in space is different. Is it possible to align model A exactly like model B by rotating it? The answer is no. The reason for that is if we rotate A the arrangement of other group gets disturbed as shown below;

We cannot make the spatial arrangement of A and B exactly the same by rotating them in any direction. A and B is said to be non-superimposable because we cannot make them look exactly.

Let us now see what will happen if a molecule containing two same groups attached to a central carbon atom is rotated as shown in the figure below;

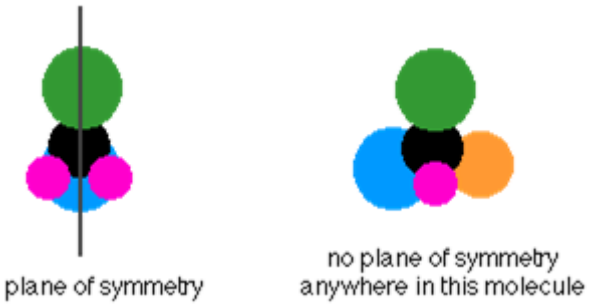
Rotating molecule A by 180 degrees will give the same arrangement of the atom as that of B as shown below;

From the above explanation, we can conclude that the compound will be optically active only if all the group attached to the central carbon atom are different.

Chiral and Achiral Molecules

The difference between chiral and achiral molecules can be explained on the basis of the plane of symmetry. If all the attached group to the central carbon atom are different then there is no plane of symmetry. Such a molecule is known as a chiral molecule.

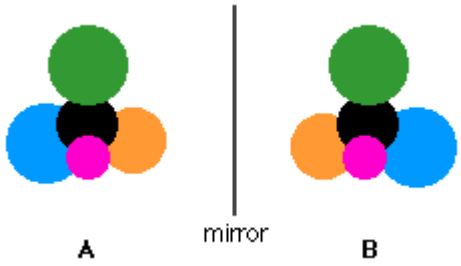
If all the group attached to the central carbon atom are not different then there exist plane of symmetry. Such molecules are called achiral molecules. It is clear that only molecule having chiral centre will show optical isomerism.



Relationship Between The Enantiomers

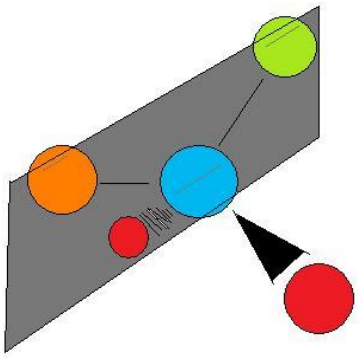
Enantiomers are a type of stereoisomers in which two molecules are a non-superimposable mirror image of each other.

In other words, one of the enantiomers is a mirror image of the other which cannot be superimposed. In other words, if a mirror looks at one isomer, it would see the other. The two isomers (the original and its mirror image) have a different spatial arrangement.



Chirality

Chirality essentially means 'mirror-image, non-superimposable molecules', and to say that a molecule is chiral is to say that its mirror image (it must have one) is not the same as it self. Whether a molecule is chiral or achiral depends upon a certain set of overlapping conditions. Figure 4 shows an example of two molecules, chiral and achiral, respectively. Notice the distinct characteristic of the achiral molecule: it possesses two atoms of same element. In theory and reality, if one were to create a plane that runs through the other two atoms, they will be able to create what is known as bisecting plane: The images on either side of the plan is the same as the other (Figure).



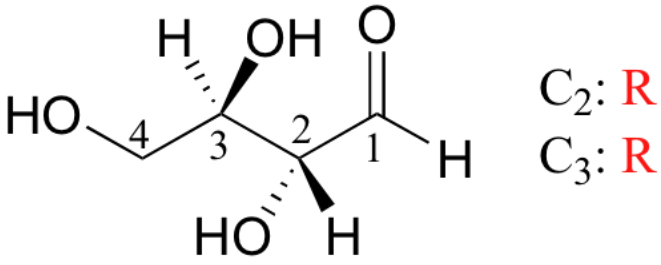
Figure

In this case, the molecule is considered 'achiral'. In other words, to distinguish chiral molecule from an achiral molecule, one must search for the existence of the bisecting plane in a molecule. All chiral molecules are deprive of bisecting plane, whether simple or complex.

As a universal rule, no molecule with different surrounding atoms are achiral. Chirality is a simple but essential idea to support the concept of stereoisomerism, being used to explain one type of its kind. The chemical properties of the chiral molecule differs from its mirror image, and in this lies the significance of chilarity in relation to modern organic chemistry.

Compounds with Multiple Chiral Centers

We turn our attention next to molecules which have more than one stereocenter. We will start with a common four-carbon sugar called D-erythrose.

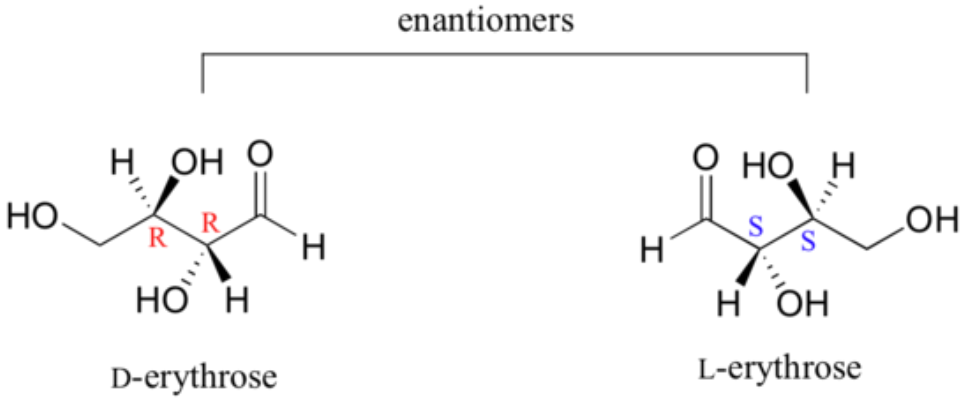


D-erythrose

A note on sugar nomenclature: biochemists use a special system to refer to the stereochemistry of sugar molecules, employing names of historical origin in addition to the designators '*D*' and '*L*'. You will learn about this system if you take a biochemistry class. We

will use the *D/L* designations here to refer to different sugars, but we won't worry about learning the system.

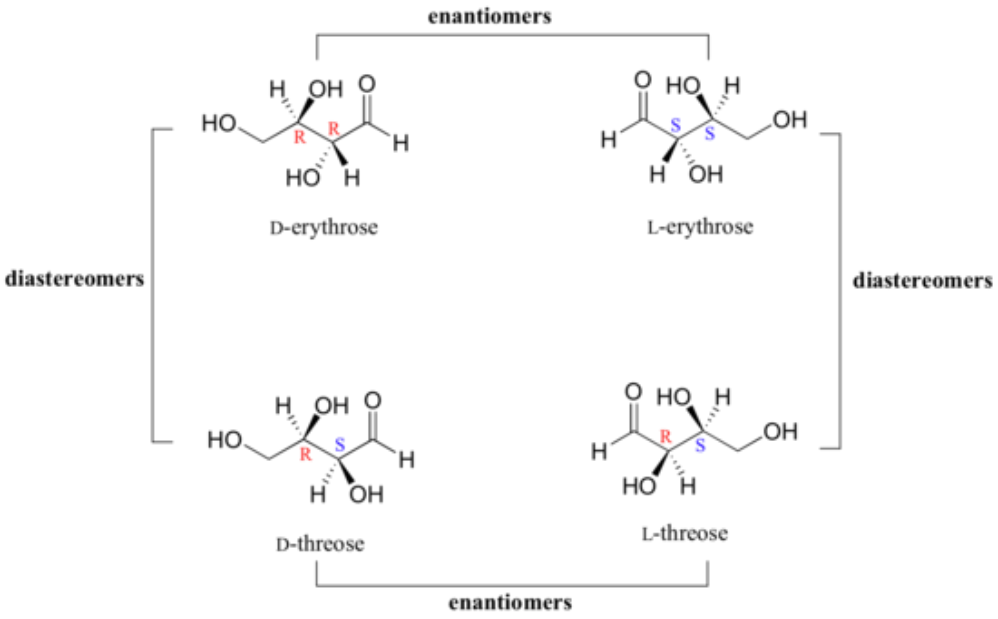
As you can see, *D*-erythrose is a chiral molecule: C_2 and C_3 are stereocenters, both of which have the *R* configuration. In addition, you should make a model to convince yourself that it is impossible to find a plane of symmetry through the molecule, regardless of the conformation. Does D-erythrose have an enantiomer? Of course it does – if it is a chiral molecule, it must. The enantiomer of erythrose is its mirror image, and is named L-erythrose (once again, you should use models to convince yourself that these mirror images of erythrose are not superimposable).



D-erythrose L-erythrose

Notice that both chiral centers in L-erythrose both have the *S* configuration. *In a pair of enantiomers,* **all** *of the chiral centers are of the opposite configuration.*

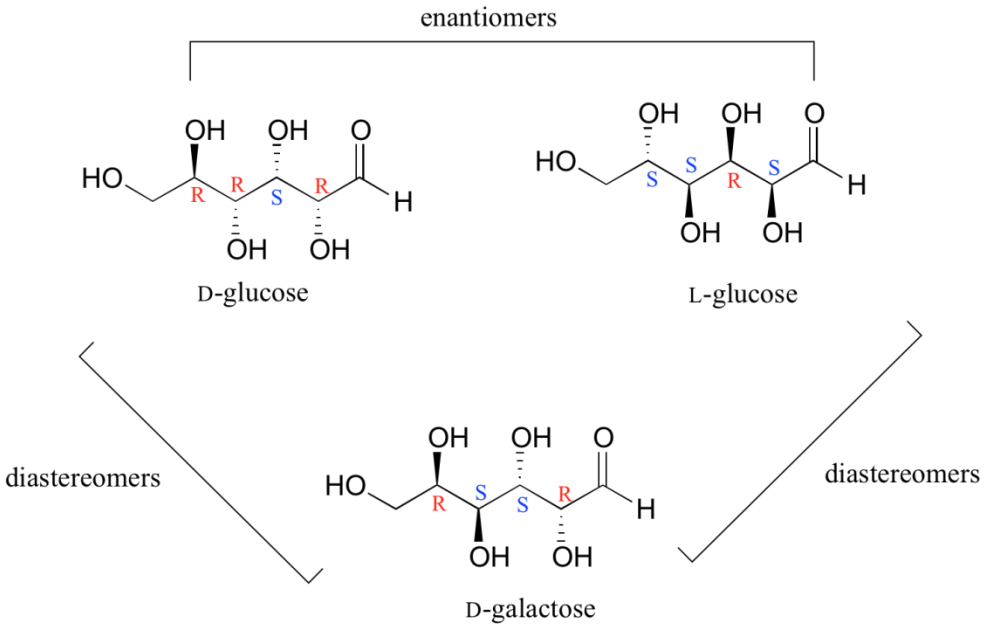
What happens if we draw a stereoisomer of erythrose in which the configuration is *S* at C_2 and *R* at C_3? This stereoisomer, which is a sugar called D-threose, is *not* a mirror image of erythrose. D-threose is a **diastereomer** of both D-erythrose and L-erythrose.



The definition of diastereomers is simple: if two molecules are stereoisomers (same molecular formula, same connectivity, different arrangement of atoms in space) but are *not* enantiomers, then they are diastereomers by default. *In practical terms, this means that at least one - but not all - of the chiral centers are opposite in a pair of diastereomers.* By definition, two molecules that are diastereomers are *not* mirror images of each other.

L-threose, the enantiomer of D-threose, has the *R* configuration at C_2 and the *S* configuration at C_3. L-threose is a diastereomer of both erythrose enantiomers.

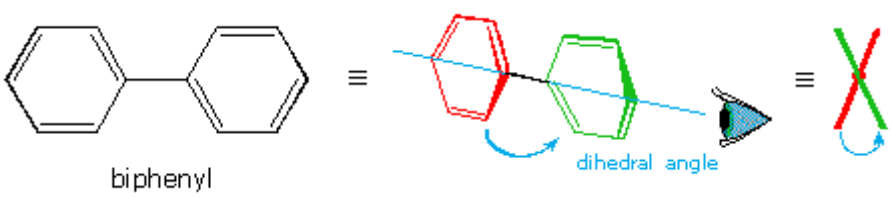
In general, a structure with *n* stereocenters will have 2^n different stereoisomers. (We are not considering, for the time being, the stereochemistry of double bonds – that will come later). For example, let's consider the glucose molecule in its open-chain form (recall that many sugar molecules can exist in either an open-chain or a cyclic form). There are two enantiomers of glucose, called D-glucose and L-glucose. The D-enantiomer is the common sugar that our bodies use for energy. It has $n = 4$ stereocenters, so therefore there are $2^n = 2^4 = 16$ possible stereoisomers (including D-glucose itself).

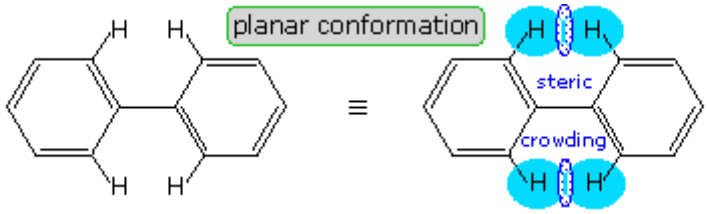


In L-glucose, all of the stereocenters are inverted relative to *D*-glucose. That leaves 14 diastereomers of D-glucose: these are molecules in which at least one, but not all, of the stereocenters are inverted relative to D-glucose. One of these 14 diastereomers, a sugar called *D*-galactose, is shown above: in D-galactose, one of four stereocenters is inverted relative to D-glucose. Diastereomers which differ in only one stereocenter (out of two or more) are called **epimers**. D-glucose and D-galactose can therefore be refered to as epimers as well as diastereomers.

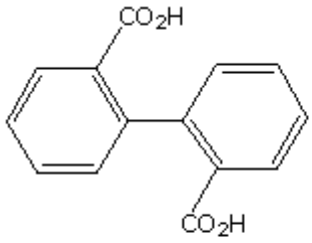
Biphenyl

Another class of compounds that display conformational enantiomorphism are the substituted biphenyls. As shown in the following diagram, biphenyl itself is not planar, one benzene ring being slightly twisted or canted in relation to the other as a consequence of steric crowding. This crowding will be demonstrated by clicking on the diagram. The resulting chiral conformation, having a dihedral angle of about 45º, equilibrates rapidly with its enantiomer by rotation about the connecting single bond. Note that a conformation having a 90º dihedral angle is achiral, as a consequence of a plane of symmetry.

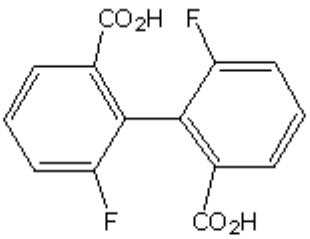




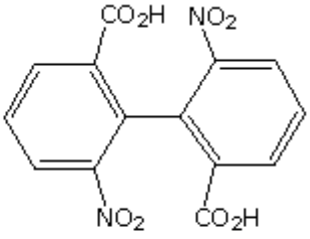
If each of the phenyl rings of a biphenyl has two different ortho or meta substituents (one may be hydrogen), even the twisted 90º dihedral angle conformer becomes chiral. In order to interconvert such conformers with their mirror image structures, a rotation through the higher energy coplanar form must be made. The ease with which this interconversion occurs will depend on the size of the ortho substituents, since these groups must slide past each other. The 2,2'-dicarboxylic acid on the left below cannot be resolved at room temperature, since thermal (kinetic) energy is sufficient to provide the necessary activation energy for racemization. The two additionally substituted diacids to its right have a higher activation energy for racemization, and can be resolved if care is taken to avoid heating them. As a rule, an activation energy barrier of 16 to 19 kcal/mole is required to prevent spontaneous room temperature racemization of substituted biphenyls. Since fluorine is smaller than a nitro group, the center compound racemizes more rapidly on heating than does the nitro compound to its right. Conformational isomers that are isolable due to high energy barriers are called **atropisomers**.



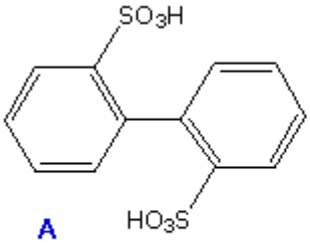
not resolved at room temperature



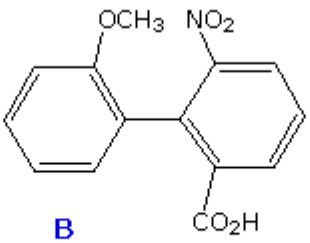
resolved at room temperature
racemizes easily



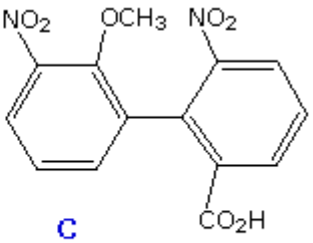
resolved at room temperature
racemizes slowly



A

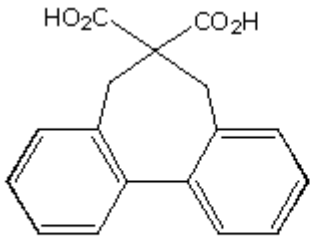


B

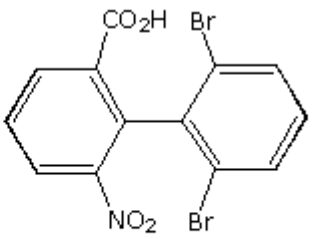


C

B racemizes 200 times faster than **C**



resolved at room temperature



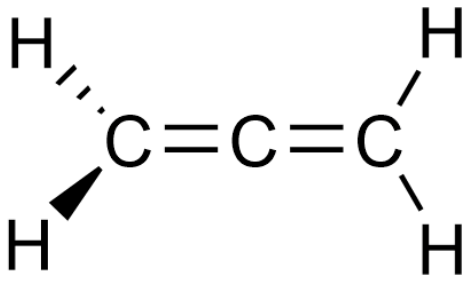
twisted conformers are not chiral
cannot be resolved

The 2,2'-disulfonic acid (compound **A**) can be resolved with care, confirming the larger size of SO_3H compared with CO_2H. Compounds **B** and **C** provide additional insight into the racemization of biphenyls. Although these biphenyls have identical ortho substituents, the meta nitro substituent adjacent to the methoxyl group in **C** exerts a buttressing influence that increases the effective size of that ortho substituent.

Finally, by clicking on the diagram a second time two additional examples of substituted biphenyls will be shown. The left hand compound is held in a twisted conformation by the bridging carbon chain. Racemization requires passing through a planar configuration, and the increased angle and eclipsing strain in this structure contribute to a large activation energy. Consequently, this compound is easily resolved into enantiomeric stereoisomers. The right hand compound is heavily ortho-substituted and most certainly resists assuming a planar configuration. However, the right benzene ring has two identical ortho substituents, so the stable 90º dihedral angle conformer has a plane of symmetry. All chiral twisted conformers are present as racemates, so this compound cannot be resolved.

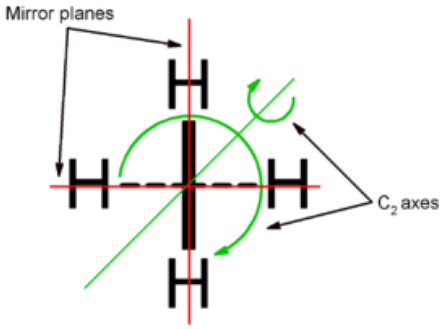
Allenes

Allenes are organic compounds in which one carbon atom has double bonds with each of its two adjacent carbon centres. Allenes are classified as cumulated dienes. The parent compound of this class is propadiene, which is itself also called *allene*. Compounds with an allene-type structure but with more than three carbon atoms are members of a larger class of compounds called cumulenes with X=C=Y bonding.

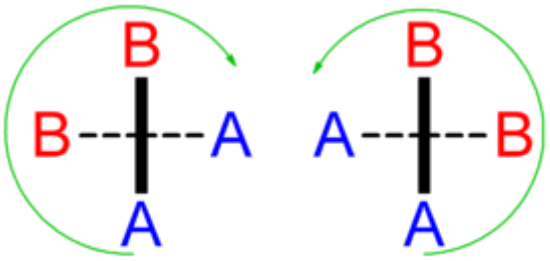


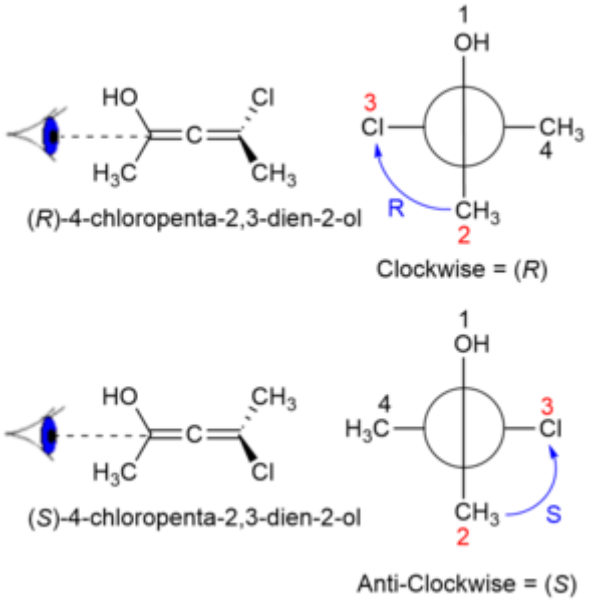
Geometry

The central carbon atom of allenes from two sigma bonds and two pi bonds. The central carbon is sp hybridized, and the two terminal carbon atoms are sp^2 hybridized. The bond angle formed by the three carbon atoms is 180˚, indicating linear geometry for the central carbon atom. The two terminal carbon atoms are planar, and these planes are twisted 90˚ from each other. The structure can also be viewed as an "extended tetrahedral" with a similar shape to methane, an anaogy that is continued into the stereochemical analysis of certain derivative molecules.



The symmetry and isomerism of allenes has long fascinated organic chemists. For allenes with four identical substituents, there exist two twofold axes of rotation through the center carbon, inclined at 45° to the CH_2 planes at either end of the molecule. The molecule can thus be thought of as a two-bladed propeller. A third twofold axis of rotation passes through the C=C=C bonds, and there is a mirror plane passing through both CH_2 planes. Thus this class of molecules belong to the D_{2d} point group. Because of the symmetry, an unsubstituted allene has no net dipole moment.





R and *S* configurations are determined by precedences of the groups attached to the axial section of the molecule when viewed along that axis. The front plane is given higher priority over the other and the final assignment is given from priority 2 to 3 (i.e. the relationship between the two planes).

An allene with two different substituents on each of the two carbon atoms will be chiral because there will no longer be any mirror planes. The chirality of these types of allenes was first predicted in 1875 by Jacobus Henricus van 't Hoff, but not proven experimentally until 1935. Where **A** has a greater priority than **B** according to the Cahn–Ingold–Prelog priority rules, the configuration of the axial chirality can be determined by considering the substituents on the front atom followed by the back atom when viewed along the allene axis. For the back atom, only the group of higher priority need be considered.

UNIT - II

2 Marks

20. State Grotthus draper law
21. State Stark – Einstein law
22. Define : Lambert law
23. Define : Beer's lambert law
24. What is mean by quantum yield
25. Draw the jablonski energy diagram
26. What is mean by photo oxidation? Give one reaction.
27. Define : Photo sensitization
28. Write the any two example of photo addition reaction
29. Define: Photo oxidiser

5 Marks

30. Write the mechanism of Norrish I reaction.
31. Write the mechanism of Norrish II reaction.
32. Discuss the jablonski energy diagram.
33. Write a short note on photooxidation reaction.
34. Write the mechanism of barton reaction.

10 Marks

35. Explain : Lambert law and Beer's lambert law
36. Write a short note on (i) Grotthus draper law (ii) Stark – Einstein law
37. Write the mechanism of Norrish I and Norrish II reactions.
38. Explain about Photosensitization

PHOTOCHEMISTRY

Photochemistry is the branch of chemistry concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wavelength from 100 to 400 nm), visible light (400–750 nm) or infrared radiation (750–2500 nm).

Principles

In the case of photochemical reactions, light provides the activation energy. Simplistically, light is one mechanism for providing the activation energy required for many reactions. If laser light is employed, it is possible to selectively excite a molecule so as to produce a desired electronic and vibrational state. Equally, the emission from a particular state may be selectively monitored, providing a measure of the population of that state. If the chemical system is at low pressure, this enables scientists to observe the energy distribution of the products of a chemical reaction before the differences in energy have been smeared out and averaged by repeated collisions.

The absorption of a photon of light by a reactant molecule may also permit a reaction to occur not just by bringing the molecule to the necessary activation energy, but also by changing the symmetry of the molecule's electronic configuration, enabling an otherwise inaccessible reaction path, as described by the Woodward–Hoffmann selection rules. A 2+2 cycloaddition reaction is one example of a pericyclic reaction that can be analyzed using these rules or by the related frontier molecular orbital theory.

Some photochemical reactions are several orders of magnitude faster than thermal reactions; reactions as fast as 10^{-9} seconds and associated processes as fast as 10^{-15} seconds are often observed.

The photon can be absorbed directly by the reactant or by a photosensitizer, which absorbs the photon and transfers the energy to the reactant. The opposite process is called quenching when a photo exited state is deactivated by a chemical reagent.

Most photochemical transformations occur through a series of simple steps known as primary photochemical processes. One common example of these processes is the excited state proton transfer.

The Laws of Photochemistry

There are two basic laws of photochemistry. In 1817 Grotthus and later Draper stated that only that radiation which is absorbed by a substance is effective in producing a photochemical reaction. This is known as the Grotthus-Draper law. It does not follow, however, that all the light that is absorbed will produce a reaction.

A significant advance was made by Einstein and later by Stark who applied the concept of the quantum of energy to photochemical reactions of molecules. They formulated a law, known as the law of photochemical equivalence, which states that – each molecule taking pan in a reaction induced by exposure to radiant energy absorbs one quantum of radiation causing the reaction. It should be emphasized that this applies only to the primary process of light absorption. A molecule on the absorption of energy does not necessarily undergo reaction; again one activated molecule may cause the reaction of a large number of molecules through a chain mechanism.

The First Law of Photochemistry states that light must be absorbed for photochemistry to occur. This is a simple concept, but it is the foundation for performing photochemical and photobiological experiments correctly. This law also is known as the Grotthuss-Draper law, states that light must be absorbed by a compound in order for a photochemical effect to take place.

The Second Law of Photochemistry states that for each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction. This law also is known as, the Stark-Einstein law, states that for each photon of light absorbed by a chemical system, only one molecule is activated for a consequent reaction. Hence the law should not be taken as to mean that one molecule reacts for each quantum absorbed. The ratio of the number of molecules reacted to the number of quanta of radiation absorbed is called the quantum efficiency or quantum yield (Φ). i.e.,

$$\Phi = \text{[Number of molecules reacted / Number of quanta absorbed]}$$

This then is the relation between the amount which undergoes photochemical reaction and the amount of radiant energy absorbed. In an idealized system, the quantum yield should be unity. For several reactions, $\Phi = 1$, for many reactions $\Phi > 1$, while for other $\Phi < 1$.

As a matter of fact, on one from the law of photochemical equivalence arc considered to be due to one or more side-effects and explanations for these have been offered. In some cases, quantum yield of 2 is in accordance with the Einstein-Stark law. For example, the photochemical reaction between hydrogen and iodine takes place according to the following scheme:

Each quantum of absorbed radiation forms two hydrogen iodide molecules, yielding a Φ value of 2. However, in the reaction between hydrogen and chlorine θ is very large and may assume a value of 10^6. Such high values of θ definitely indicate a chain mechanism in the reaction. Several reactions are also known where θ assumes values much lower than unity. These low values are mainly due to fluorescence, phosphorescence and other side-effects. When a solution of anthracene in benzene is exposed to ultraviolet radiation, two molecules of anthracene combine to form anthracene, $2C_{14}H_{10} \rightarrow C_{28}H_{20}$. The reaction is accompanied by fluorescence and the quantum yield is low in dilute solution due to de-excitation. When the concentration of anthracene is increased in the solution the quantum yield increases whereas fluorescence decreases. At sufficiently high concentration the quantum yield assumes a limiting constant value and fluorescence practically disappears.

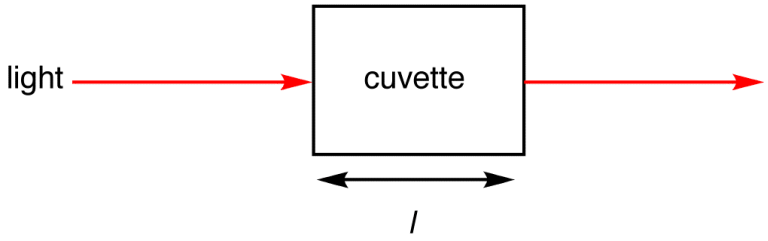
Lambert's law

Lambert's law of absorption states that equal parts in the same absorbing medium absorb equal fractions of the light that enters them. If in traversing a path of length dx the intensity is reduced from I to I – dI then Lambert's law states that dI/I is the same for all elementary paths of length dx. Thus Equation may be obtained, where K is a constant known as the absorption coefficient.

$$dI/I = -Kdx$$

Beer-Lambert law

For each wavelength of light passing through the spectrometer, the intensity of the light passing through the reference cell is measured. This is usually referred to as IoIo - that's II for Intensity.



Light absorbed by sample in a cuvette

The intensity of the light passing through the sample cell is also measured for that wavelength - given the symbol, I. If I is less than Io, then the sample has absorbed some of the light (neglecting reflection of light off the cuvette surface). A simple bit of math is then done in the computer to convert this into something called the absorbance of the sample - given the symbol, A. The absorbance of a transition depends on two external assumptions.

1. The absorbance is directly proportional to the concentration (c) of the solution of the sample used in the experiment.
2. The absorbance is directly proportional to the length of the light path (l), which is equal to the width of the cuvette.

Assumption one relates the absorbance to concentration and can be expressed a

$$A \propto c \qquad (1)$$

The absorbance (A) is defined via the incident intensity Io and transmitted intensity I by

$$A = \log_{10}(I_o/I) \qquad (2)$$

Assumption two can be expressed as

$$A \propto l \qquad (3)$$

Combining Equations 1 and 3:

$$A \propto cl \qquad (4)$$

This proportionality can be converted into an equality by including a proportionality constant (ϵ).

$$A=\epsilon cl \qquad (5)$$

This formula is the common form of the *Beer-Lambert Law*, although it can be also written in terms of intensities:

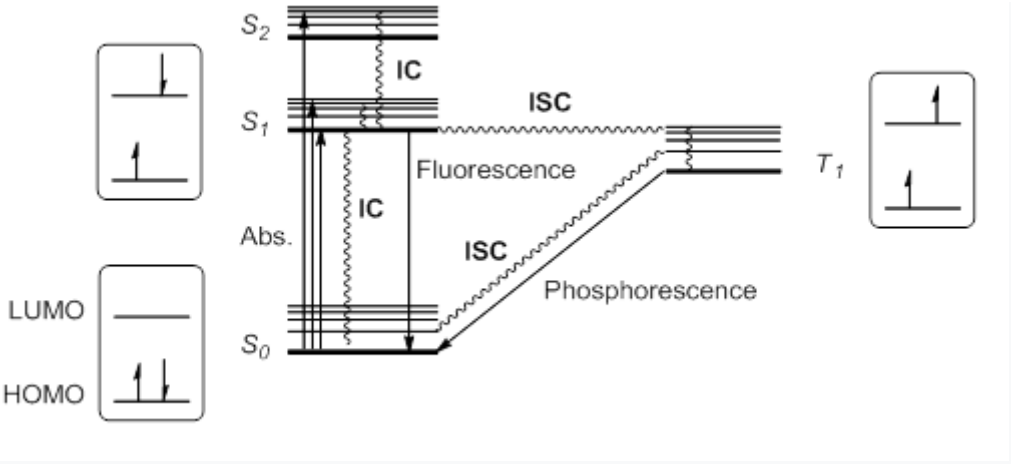
$$A=\log_{10}(I_o/I)=\epsilon lc \qquad (6)$$

The constant $\epsilon\epsilon$ is called **molar absorptivity** or **molar extinction coefficient** and is a measure of the probability of the electronic transition. On most of the diagrams you will come across, the absorbance ranges from 0 to 1, but it can go higher than that. An absorbance of 0 at some wavelength means that no light of that particular wavelength has been absorbed. The intensities of the sample and reference beam are both the same, so the ratio Io/I is 1 and the log10 of 1 is zero.

Fluorescence and phosphorescence

When a molecule or atom in the ground state (S_0) absorbs light, one electron is excited to a higher orbital level. This electron maintains its spin according to the spin selection rule; other transitions would violate the law of conservation of angular momentum. The excitation to a higher singlet state can be from HOMO to LUMO or to a higher orbital, so that singlet excitation states S_1, S_2, S_3… at different energies are possible.

Kasha's rule stipulates that higher singlet states would quickly relax by radiationless decay or internal conversion (IC) to S_1. Thus, S_1 is usually, but not always, the only relevant singlet excited state. This excited state S_1 can further relax to S_0 by IC, but also by an allowed radiative transition from S_1 to S_0 that emits a photon; this process is called fluorescence.



Jablonski diagram. Radiative paths are represented by straight arrows and non-radiative paths by curly lines.

Alternatively, it is possible for the excited state S_1 to undergo spin inversion and to generate a triplet excited state T_1 having two unpaired electrons with the same spin. This violation of the spin selection rule is possible by intersystem crossing (ISC) of the vibrational and electronic levels of S_1 and T_1. According to Hund's rule of maximum multiplicity, this T_1 state would be somewhat more stable than S_1.

This triplet state can relax to the ground state S_0 by radiationless IC or by a radiation pathway called phosphorescence. This process implies a change of electronic spin, which is forbidden by spin selection rules, making phosphorescence (from T_1 to S_0) much slower than fluorescence (from S_1 to S_0). Thus, triplet states generally have longer lifetimes than singlet states. These transitions are usually summarized in a state energy diagram or Jablonski diagram, the paradigm of molecular photochemistry.

These excited species, either S_1 or T_1, have a half empty low-energy orbital, and are consequently more oxidizing than the ground state. But at the same time, they have an electron in a high energy orbital, and are thus more reducing. In general, excited species are prone to participate in electron transfer processes.

Photo-oxidation

Photo-oxidation is the degradation of a polymer surface in the presence of oxygen or ozone, facilitated by radiant energy such as UV or artificial light. This process is the most significant factor in weathering of polymers. Photo-oxidation is a chemical change that reduces the polymer's molecular weight. As a consequence of this change the material becomes more brittle, with a reduction in its tensile, impact and elongation strength. Discoloration and loss of surface smoothness accompany photo-oxidation. High temperature

and localized stress concentrations are factors that significantly increase the effect of photo-oxidation.

Mechanism

Aldehydes, ketones and carboxylic acids along or at the end of polymer chains are generated by oxygenated species in photolysis of photo-oxidation. The initiation of photo-oxidation reactions is due to the existence of chromophoric groups in the macromolecules. Photo-oxidation can occur simultaneously with thermal degradation and each of these effects can accelerate the other.

The photo-oxidation reactions include chain scission, cross linking and secondary oxidative reactions. The following process steps can be considered:[1] initial step, chain propagation step, chain branching and termination step. In the initial step, free radicals are formed by photon absorption. In the chain propagation step, a free radical reacts with oxygen to produce a polymer peroxy radical (POO•). This reacts with a polymer molecule to generate polymer hydroperoxide (POOH) and a new polymer alkyl radical (P•). With chain branching, polymer oxy radicals (PO•) and hydroxy radicals (HO•) are formed by photolysis. The termination step is cross linking which is a result of the reaction of different free radicals with each other.

Initial step

$$\text{Polymer} \longrightarrow \text{P•} + \text{P•}$$

Chain propagation

$$\text{P•} + O_2 \longrightarrow \text{POO•}$$

$$\text{POO•} + \text{PH} \longrightarrow \text{POOH} + \text{P•}$$

Chain branching

$$\text{POOH} \longrightarrow \text{PO•} + \text{OH•}$$

$$\text{PH} + \text{OH•} \longrightarrow \text{P•} + H_2O$$

$$\text{PO•} \longrightarrow \text{Chain scission reactions}$$

Termination

$$\text{POO•} + \text{POO•} \longrightarrow \text{Cross linking reaction to non radical product}$$

$$\text{POO•} + \text{P•} \longrightarrow \text{Cross linking reaction to non radical product}$$

$$\text{P•} + \text{P•} \longrightarrow \text{Cross linking reaction to non radical product}$$

where

PH = Polymer

P• = Polymer alkyl radical

PO• = Polymer oxy radical (Polymer alkoxy radical)

POO• = Polymer peroxy radical (Polymer alkylperoxy radical)

POOH = Polymer hydroperoxide

OH• = hydroxy radical

Effects of dyes/pigments

Adding pigment light absorbers and photostabilizers (UV absorbers) is one way to minimise photo-oxidation in polymers. Antioxidants are used to inhibit the formation of hydroperoxides in the photo-oxidation process.

Dyes and pigments are used in polymer materials to provide color changing properties. These additives can reduce the rate of polymer degradation. Cu-phthalocyanine dye can help stabilize against degradation, but in other situations such as photochemical aging can actually accelerate degradation. The excited Cu-phthalocyanine may abstract hydrogen atoms from methyl groups in the PC, which increase the formation of free radicals. This acts as the starting points for the sequential photo-oxidation reactions leading to the degradation of the PC.

Electron transfer sensitization is a mechanism where the excited Cu-phthalocyanine abstracts electrons from PC to form Cu-Ph radical anion and PC radical cations. These species in the presence of oxygen can cause oxidation of the aromatic ring.

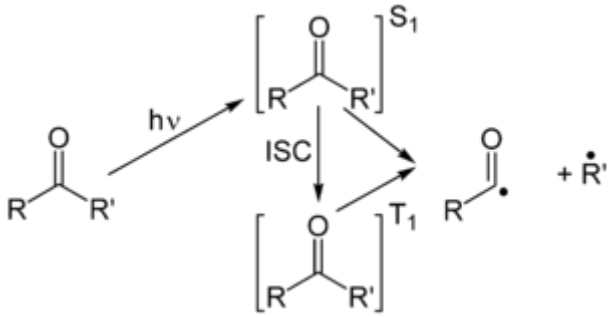
Norrish reaction

The Norrish reaction in organic chemistry describes the photochemical reactions taking place with ketones and aldehydes. This type of reaction is subdivided in Norrish type I reactions and Norrish type II reactions. The reaction is named after Ronald George Wreyford Norrish. While of limited synthetic utility these reactions are important in the photo-oxidation of polymers such as polyolefins, certain polycarbonates and polyketones.

Norrish type I reaction

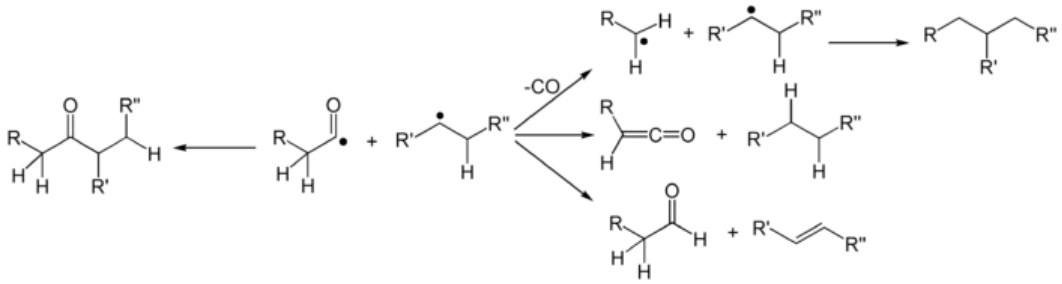
The Norrish type I reaction is the photochemical cleavage or homolysis of aldehydes and ketones into two free radical intermediates (α-scission). The carbonyl group accepts a photon and is excited to a photochemical singlet state. Through intersystem crossing the triplet state can be obtained. On cleavage of the α-carbon bond from either state,

two radical fragments are obtained. The size and nature of these fragments depends upon the stability of the generated radicals; for instance, the cleavage of 2-butanone largely yields ethyl radicals in favour of less stable methyl radicals.



Several secondary reaction modes are open to these fragments depending on the exact molecular structure.

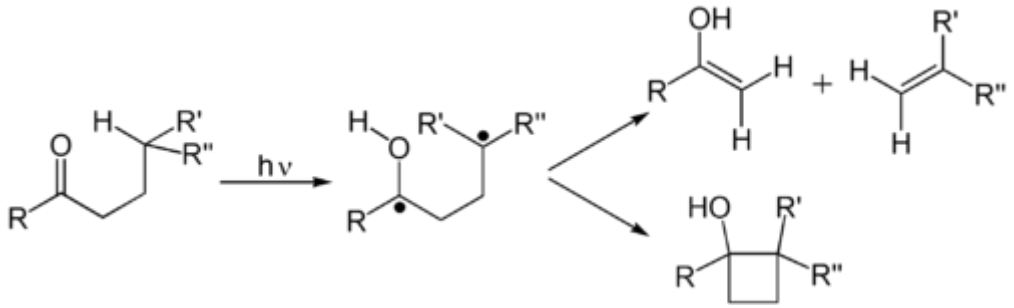
- The fragments can simply recombine to the original carbonyl compound, with racemisation at the α-carbon.
- The acyl radical can lose a molecule of carbon monoxide, forming a new carbon radical at the other α-carbon, followed by formation of a new carbon–carbon bond between the radicals. The ultimate effect is simple extraction of the carbonyl unit from the carbon chain. The rate and yield of this product depends upon the bond-dissociation energy of the ketone's α substituents. Typically the more α substituted a ketone is, the more likely the reaction will yield products in this way.
- The abstraction of an α-proton from the carbonyl fragment may form a ketene and an alkane.
- The abstraction of a β-proton from the alkyl fragment may form an aldehyde and an alkene.



Norrish type II reaction

A Norrish type II reaction is the photochemical intramolecular abstraction of a γ-hydrogen (a hydrogen atom three carbon positions removed from the carbonyl group) by the

excited carbonyl compound to produce a 1,4-biradical as a primary photoproduct.[8] Norrish first reported the reaction in 1937.



Secondary reactions that occur are fragmentation (β-scission) to form an alkene and an enol (which will rapidly tautomerise to a carbonyl), or intramolecular recombination of the two radicals to a substituted cyclobutane.

Photosensitization

Photosensitization is the process by which a photochemical or photophysical alteration occurs in one molecular entity as a result of initial absorption of radiation by another molecular entity called a *photosensitizer*. In mechanistic photochemistry the term is limited to cases in which the photosensitizer is not consumed in the reaction.

The photosensitization phenomenon can be applied to many fields such as that of photocatalysis where light is used to activate a substance, the photocatalyst, which modifies the rate of a chemical reaction without being involved itself in the chemical transformation. Within the numerous areas in which the concept of photosensitization can be applied, the contents here will be related to the biological subject. Thus, photosensitization is the process whereby a molecule activated by light is able to induce photoreactions in the biomolecules present in its environment (see Figure 1). The process is generally associated with the absorption of normal and harmless doses of light by a "strange" molecule (photosensitizer, PS) in non-harmful concentrations, reaching the absorbed energy to the constituents of tissues and cells. In the absence of this substance, the system is not affected by light provided that direct light absorption is not possible. In humans, the eyes and skin are the main receptors of light. In most cases, photosensitized reactions in the skin give rise to adverse side effects. In fact, the photosensitizing deoxyribonucleic acid (DNA) damage by xenobiotics has attracted considerable attention because it can involve a more extended active fraction of the solar spectrum with carcinogenic potential. In that way, the risk of biomolecules damage is

considerably increased. However, photosensitization can also be used for therapeutic purposes, what is called photodynamic therapy (PDT).

Photosensitizers are photochemically activated, and there is no direct absorption of light by biomolecules. The light that activates most photosensitizers falls under the UVA range, although there are also some substances whose spectrum of action extends to UVB. On the other hand, UVA radiation penetrates deeper into the skin and reaches these molecules, which are distributed in the deeper levels of cutaneous tissue. The main source of UVA radiation is the sun, but it is also emitted by artificial light sources, such as tanning lamps and fluorescent lights, the latter to a lesser degree.

Sun-induced skin reactions have been increasing in recent decades, due not only to social causes such as tanning, but also to the high number of photosensitizing products commonly used by contact or ingestion, which are found in plants, pharmaceuticals, food additives, chemical fertilizers, dyes, sunscreens, cosmetics, etc. This phenomenon attracts, more and more, the interest of dermatologists, the pharmaceutical industry and legislative bodies involved in the topic. Changing living habits in developed countries leads to a frequent combination of light and chemicals.

Cutaneous photosensitizers may be (a) exogenous, foreign chemicals introduced into the skin by topical or parenteral route, or (b) endogenous, biomolecules (DNA and melanin, for example) in high concentrations or metabolites. Drugs are the major exogenous source of photosensitizing reactions in the skin.

In photosensitized reactions, photons of UV or visible radiation are absorbed by a photosensitizer that is excited by light to a state rich in energy giving rise to reactions that produce a chemical alteration of a second molecule of the system (substrate), as it is shown in Figure 2. Photosensitized reactions are mediated by the excited and short-lived electronic states of the photosensitizer. Most photosensitized reactions are complex and involve several competitive reaction paths.

The primary photophysical processes of a photosensitizer are as follows: All chemical photosensitizers, before excitation, exist in their lowest energy state (ground state, S00). By absorption of a photon, an electron of the sensitizer is promoted to a higher empty molecular orbital (LUMO) without change in the total spin (Wigner's law), giving rise (after processes of vibrational relaxation and interaction with the solvent) to the first excited state S11 that, as the ground state, is singlet. Very few photosensitized reactions occur from this state due to its

very short lifetime (≈1-100 ns).The photosensitizer singlet excited state can be deactivated by means of 4 processes, which compete with each other: i) decaying directly to the ground state by emitting heat (by internal conversion of the electronic energy to the vibrational energy, IC); ii) emitting light (fluorescence), Iii) by ionization giving an electron and the radical cation of the photosensitizer or, iv) by intersystem crossing (ISC) with spin inversion, to the lowest triplet excited state, T11.

Barton reaction

The **Barton reaction**, also known as the **Barton nitrite ester reaction**, is a photochemical reaction that involves the photolysis of an alkyl nitrite to form a δ-nitroso alcohol.

Discovered in 1960, the reaction is named for its discoverer, Nobel Laureate Sir Derek Barton. Barton's Nobel Prize in Chemistry in 1969 was awarded for his work on understanding conformations of organic molecules, work which was key to realizing the utility of the Barton Reaction.

The Barton reaction involves a homolytic RO–NO cleavage, followed by δ-hydrogen abstraction, free radical recombination, and tautomerization to form an oxime. Selectivity for the δ-hydrogen is a result of the conformation of the 6-membered radical intermediate. Often, the site of hydrogen atom abstraction can be easily predicted. This allows the regio- and stereo-selective introduction of functionality into complicated molecules with high yield. Due to its unique property at the time to change otherwise inert substrates, Barton used this reaction extensively in the 1960s to create a number of unnatural steroid analogues.

While the Barton reaction has not enjoyed the popularity or widespread use of many other organic reactions, together with the mechanistically similar Hofmann–Löffler reaction it represents one of the first examples of C-H activation chemistry, a field which is now the topic of much frontline research in industrial and academic chemistry circles.

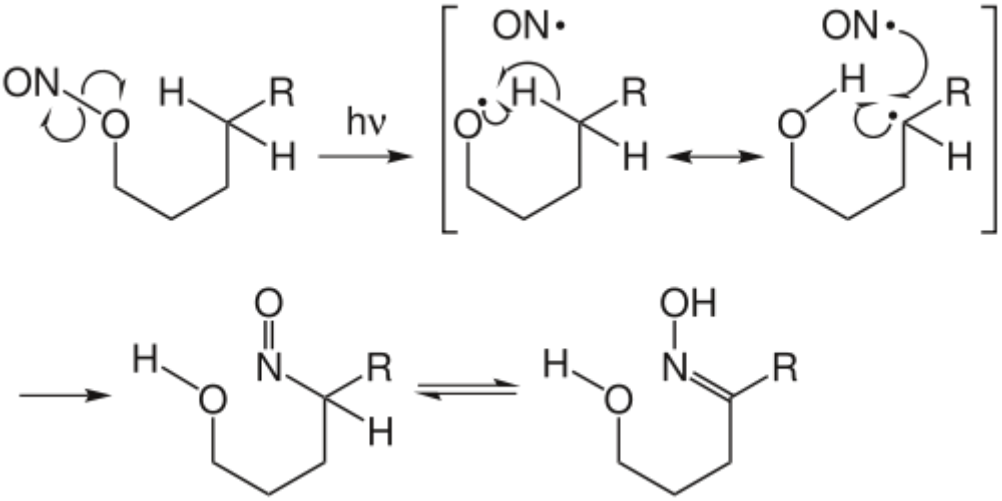
The unusual alkyl nitrite starting material of the Barton reaction is prepared by attack of an alcohol on a nitrosylium cation generated in situ by dehydration of doubly protonated nitrous acid. This series of steps is mechanistically identical to the first half of the mechanism formation of the more well-known aryl and alkyl diazonium salts.

While the synthesis of alkyl nitrites from nitrosyl chloride is known and oft-employed in the context of complex molecule synthesis, the reaction is reversible and the products are in thermodynamic equilibrium with the starting material. Furthermore, nitrosyl chloride is a

powerful oxidizing agent, and oxidation of the alcohols with concomitant chlorination has been observed. The reaction of nitrosyl chloride with aromatic alcohols generally yields nitroso compounds and other over-oxidation products.

Mechanism

The Barton reaction commences with a photochemically induced cleavage of the nitrite O-N bond, typically using a high pressure mercury lamp. This produces an alkyoxyl radical which immediately abstracts a hydrogen atom from the δ-carbon. In the absence of other radical sources or other proximal reactive groups, the alkyl radical recombines with the nitrosyl radical. The resultant nitroso compounds undergoes tautomerization to the isolated oxime product.



The carbon centered radical can be intercepted by other radical sources such as iodine or acrylonitrile. The first instance results in the δ-hydrogen being replaced with iodine, then subsequent cyclization to a tetrahydrofuran by an SN2 reaction. The second example results in a chain elongation product with the oxime formed 2 carbon units further from the oxygen than normal.

This mechanistic hypothesis is supported by kinetic isotope effect experiments. Isotopic labeling of the nitrite with 15N has shown the mechanism non-'caged' and that the nitrosyl radical formed from a given nitrite recombines randomly with other alkyl radicals. However, recombination of the nitrosyl radical with the alkoxyl radical (a reversal of the homolytic cleavage) has been shown to proceed without scrambling of isotope labels. This lack of tight radical pairing is also supported by the observation that alkyl radicals generated by Barton conditions can undergo radical cyclization while analogous intermediates generated by lead tetraacetate oxidation do not.

In rare cases, it appears that the alkoxyl radical may epimerize before hydrogen atom abstraction.

Most commonly, including steroidal systems, the hydrogen atom is abstracted from a methyl group that has a 1,3 diaxial relationship with the alkoxyl radical. In the absence of a hydrogen on the δ-carbon, or when the particular conformation of the substrate orients the ε-carbon close together, 1,6-hydrogen atom transfer is the favored process. However, these reactions tend to be an order of magnitude slower than the corresponding 1,5-hydrogen atom transfer.

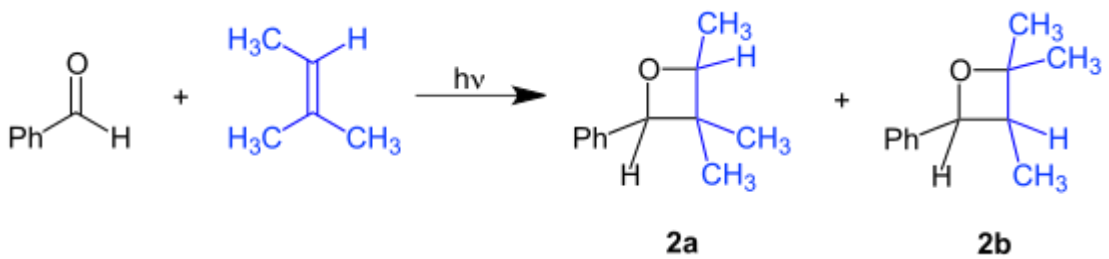
Computational studies have shown that this preference for 1,5-hydrogen atom transfer over 1,6-hydrogen atom transfer appears to be entropically favored rather than a result of a particular stable 'chair-like' transition state.[16] In fact, it has been calculated that the 1,6-hydrogen atom transfer proceeds through a transition that is about 0.8 kcal/mol lower than that of the 1,5.

In acyclic systems, δ-hydrogen abstraction is still observed, however, alpha-hydrogen abstraction to form the corresponding ketone competes.

In certain cases, particularly nitrites derived from cyclopentyl alcohols, the oxygen-centered radical prefers to react via C-C bond cleavage as opposed to H-atom abstraction. For example, when subjected to Barton conditions, cyclopentyl nitrite forms glutaraldehyde monoxime. This is also observed in cases where the radical intermediate formed by fragmentation is particularly stable, such as the allylic radical formed by the fragmentation of isopulegol nitrite.

Paternò–Büchi reaction

The Paternò–Büchi reaction, named after Emanuele Paternò and George Büchi who established its basic utility and form, is a photochemical reaction that forms four-membered oxetane rings from an excited carbonyl and reacting with an alkene. With substrates benzaldehyde and 2-methyl-2-butene the reaction product is a mixture of structural isomers:



2a **2b**

Another substrate set is benzaldehyde and furan

The alternative strategy for the above reaction is called the Transposed Paternò−Büchi reaction.