GOVERNMENT ARTS AND SCIENCE COLLEGE
(Affiliated to Manonmaniam Sundaranar University, Tirunelveli.)
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STUDY MATERIAL FOR B.SC CHEMISTRY

ORGANIC CHEMISTRY-1

SEMESTER – II

Academic Year 2022-2023

Prepared by

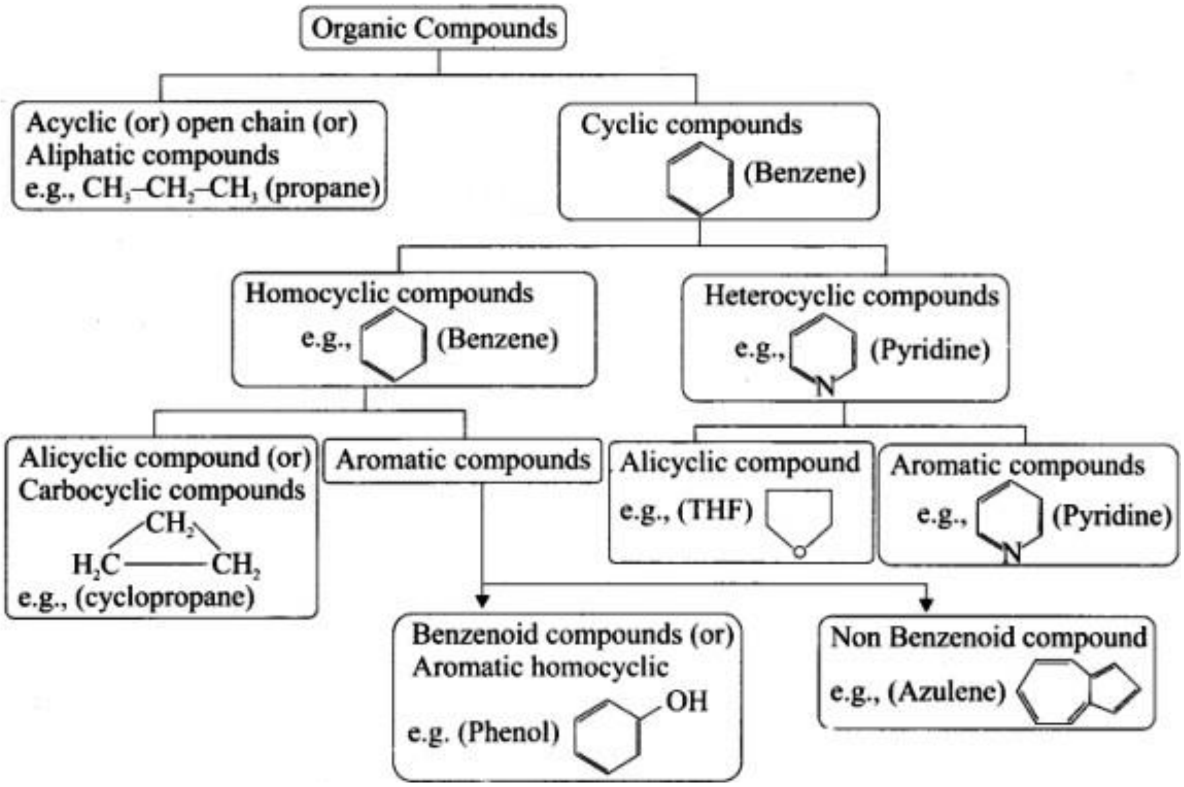
CHEMISTRY DEPARTMENT

UNIT-1

BASIC CONCEPTS

Classification of organic compounds

There are a large number of organic compounds and therefore a proper systematic classification was required. Organic compounds can be broadly classified as acyclic (open chain) or cyclic (closed chain).



Nomenclature of organic compounds

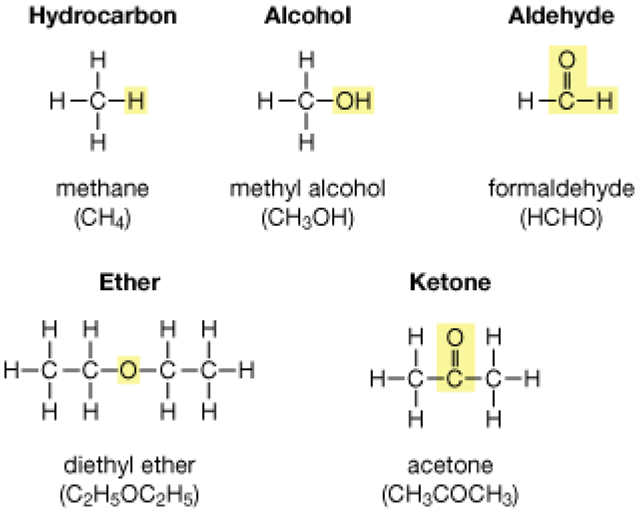
In chemical nomenclature, the IUPAC nomenclature of organic chemistry is a method of naming organic chemical compounds as recommended by the International Union of Pure and Applied Chemistry (IUPAC). It is published in the Nomenclature of Organic Chemistry (informally called the Blue Book). Ideally, every possible organic compound should have a name from which an unambiguous structural formula can be created. There is also an IUPAC nomenclature of inorganic chemistry.

The steps for naming an organic compound are:

1. Identification of the parent hydrocarbon chain. This chain must obey the following rules, in order of precedence:

- It should have the maximum number of substituents of the suffix functional group. By suffix, it is meant that the parent functional group should have a suffix, unlike halogen substituents. If more than one functional group is present, the one with highest group precedence should be used.
- It should have the maximum number of multiple bonds.
- It should have the maximum length.
- It should have the maximum number of substituents or branches cited as prefixes
- It should have the maximum number of single bonds.

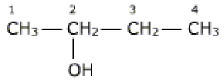
2. Identification of the parent functional group, if any, with the highest order of precedence.



3. Identification of the side-chains. Side chains are the carbon chains that are not in the parent chain, but are branched off from it.
4. Identification of the remaining functional groups, if any, and naming them by their ionic prefixes (such as hydroxy for -OH, oxy for =O, oxyalkane for O-R, etc.). Different side-chains and functional groups will be grouped together in alphabetical order. (The prefixes di-, tri-, etc. are not taken into consideration for grouping alphabetically. For example, ethyl comes before dihydroxy or dimethyl, as the "e" in "ethyl" precedes the "h" in "dihydroxy" and the "m" in "dimethyl" alphabetically. The "di" is not considered in either case). When both side chains and secondary functional groups are present, they should be written mixed together in one group rather than in two separate groups.
5. Identification of double/triple bonds.
6. Numbering of the chain. This is done by first numbering the chain in both directions (left to right and right to left), and then choosing the numbering which follows these rules, in order of precedence.

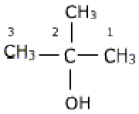
- Has the lowest-numbered locant (or locants) for the suffix functional group. Locants are the numbers on the carbons to which the substituent is directly attached.
- Has the lowest-numbered locants for multiple bonds (The locant of a multiple bond is the number of the adjacent carbon with a lower number).
- Has the lowest-numbered locants for prefixes.

7. Numbering of the various substituents and bonds with their locants. If there is more than one of the same type of substituent/double bond, a prefix is added showing how many there are (di – 2 tri – 3 tetra – 4 then as for the number of carbons below with 'a' added)



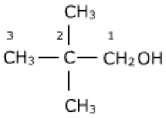
$\overset{1}{CH_3}-\underset{OH}{\overset{2}{CH_2}}-\overset{3}{CH_2}-\overset{4}{CH_3}$

But -2-ol



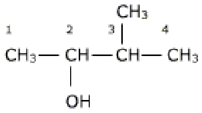
$\overset{3}{CH_3}-\underset{OH}{\overset{CH_3}{\overset{2}{C}}}-\overset{1}{CH_3}$

2 - Methylpropane - 2- ol



$\overset{3}{CH_3}-\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{1}{CH_2OH}$

2, 2 - Dimethyl propan-1-ol



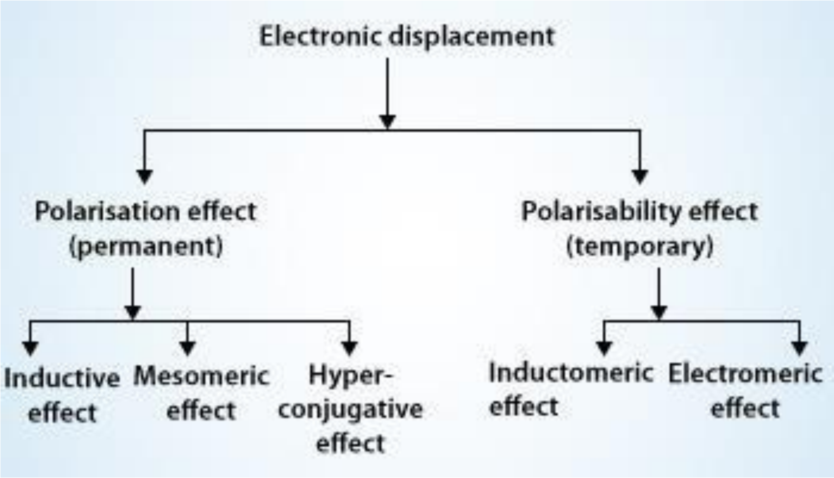
$\overset{1}{CH_3}-\underset{OH}{\overset{2}{CH}}-\overset{CH_3}{\overset{3}{CH}}-\overset{4}{CH_3}$

3 - Methylbutan-2-ol

Polar effect

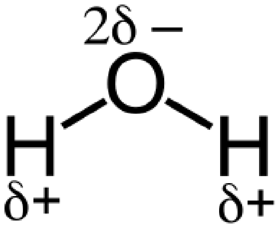
The polar effect or electronic effect in chemistry is the effect exerted by a substituent on modifying electrostatic forces operating on a nearby reaction center. The main contributors to the polar effect are the inductive effect, mesomeric effect and the through-space electronic field effect.

- Inductive electromeric effect
- Mesomeric/ Resonance effect
- Hyperconjugation effect
- Steric effct



Inductive electromeric effect

Inductive effect is observed when two atoms with different electronegativity values form the chemical bond whereas Electromeric effect occurs when a molecule having multiple bonds is exposed to an attacking agent such as a proton.



-I effect

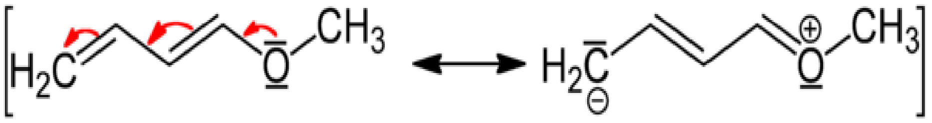
The effect of the sigma electron displacement towards the more electronegative atom by which one end becomes positively charged and the other end negatively charged is known as the inductive effect. "-I effect is a permanent effect & generally represented by an arrow on the bond."

+I effect

However, some groups, such as the alkyl group, are less electron-withdrawing than hydrogen and are therefore considered as electron-releasing. This is electron-releasing character and is indicated by the +I effect. In short, alkyl groups tend to give electrons, leading to the induction effect. However, such an effect has been questioned.

Mesomeric/ Resonance effect

The withdrawal effect or releasing effect of electrons attributed to a particular substituent through the delocalization of π or pi-electrons that can be seen by drawing various canonical structures is called a resonance effect or mesomeric effect.



The effect is used in a qualitative way and describes the electron withdrawing or releasing properties of substituents based on relevant resonance structures and is symbolized by the letter M. The mesomeric effect is negative (–M) when the substituent is an electron-withdrawing group and the effect is positive (+M) when the substituent is an electron donating group.

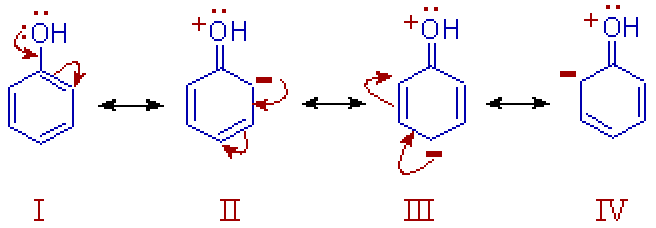
+M Effect Order

$-O^{-} > -NH_2 > -OR > -NHCOR > -OCOR > -Ph > -CH_3 > -I > -Br > -Cl > -F$

-M Effect Order

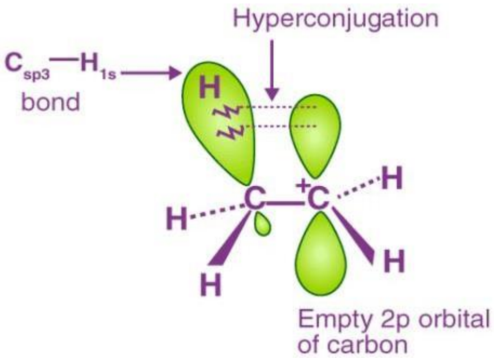
$-NO_2 > -CN > -SO_3H > -CHO > -COR > -COOCOR > -COOR > -COOH > -CONH_2 > -COO^{-}$

In phenol, the -OH group shows +M effect due to delocalization of lone pair on oxygen atom towards the ring. Thus the electron density on benzene ring is increased particularly on ortho and para positions.



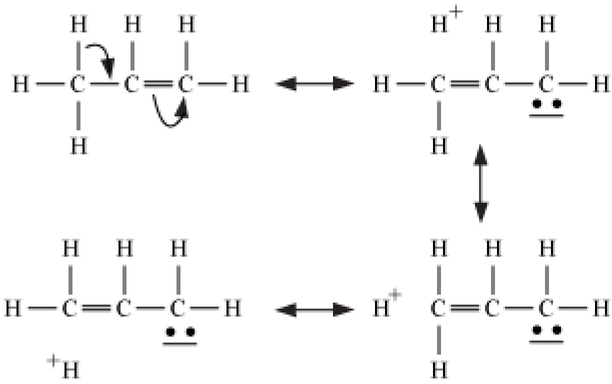
Hyperconjugation effect

In organic chemistry, hyperconjugation (σ-conjugation or no-bond resonance) refers to the delocalization of electrons with the participation of bonds of primarily σ-character. Usually, hyperconjugation involves the interaction of the electrons in a sigma (σ) orbital (e.g. C–H or C–C) with an adjacent unpopulated non-bonding p or antibonding σ* or π* orbitals to give a pair of extended molecular orbitals. However, sometimes, low-lying antibonding σ* orbitals may also interact with filled orbitals of lone pair character (n) in what is termed negative hyperconjugation. Increased electron delocalization associated with hyperconjugation increases the stability of the system. In particular, the new orbital with bonding character is stabilized, resulting in an overall stabilization of the molecule.



Propene has 4 hyperconjugation structures.

$CH_3-CH=CH_2$

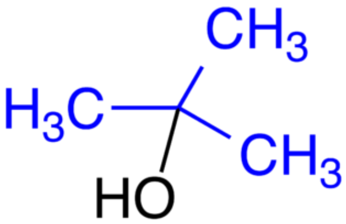


Steric effect

Steric effects are nonbonding interactions that influence the shape (conformation) and reactivity of ions and molecules. Steric effects complement electronic effects, which dictate the shape and reactivity of molecules. Steric repulsive forces between overlapping electron clouds result in structured groupings of molecules stabilized by the way that opposites attract and like charges repel.

Steric hindrance is a consequence of steric effects. Steric hindrance is the slowing of chemical reactions due to steric bulk. It is usually manifested in intermolecular reactions, whereas discussion of steric effects often focus on intramolecular interactions. Steric hindrance is often exploited to control selectivity, such as slowing unwanted side-reactions.

Steric hindrance between adjacent groups can also affect torsional bond angles. Steric hindrance is responsible for the observed shape of rotaxanes and the low rates of racemization of 2,2'-disubstituted biphenyl and binaphthyl derivatives.

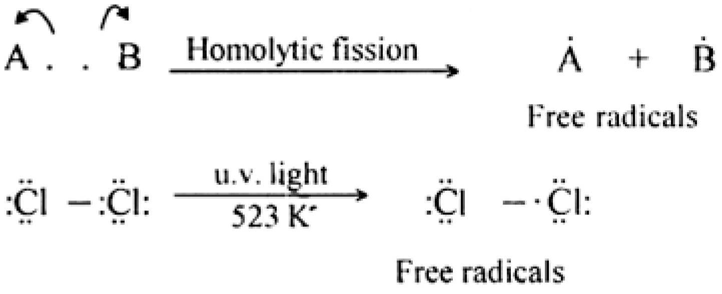


Bond fission

Bond fission is the splitting of chemical bonds. This can be generally referred to as Dissociation, when a molecule is cleaved into two or more fragments. In general, there are two classifications for bond fission: homolytic and heterolytic, depending on the nature of the process. The triplet and singlet excitation energies of a sigma bond can be used to determine if a bond will follow the homolytic or heterolytic pathway.

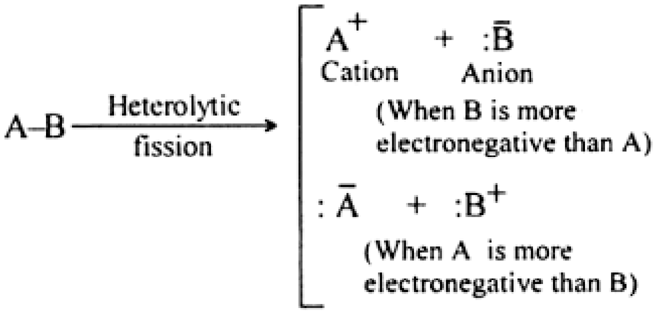
Homolytic fission

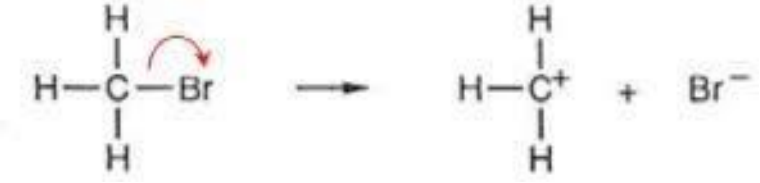
In homolytic cleavage, or homolysis, the two electrons in a cleaved covalent bond are divided equally between the products. This process is also known as homolytic fission or radical fission



Heterolytic fission

In heterolytic cleavage, or heterolysis, the bond breaks in such a fashion that the originally-shared pair of electrons remains with one of the fragments. Thus, a fragment gains an electron, having both bonding electrons, while the other fragment loses an electron. This process is also known as ionic fission.



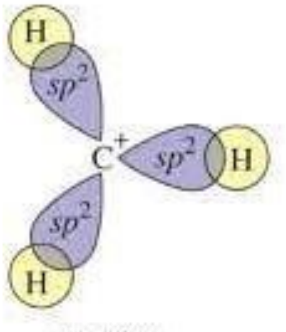


Reaction intermediate

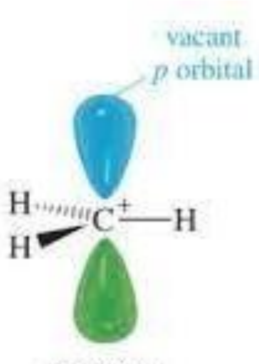
A reaction intermediate or an intermediate is a molecular entity that is formed from the reactants and reacts further to give the directly observed products of a chemical reaction. Most chemical reactions are stepwise, that is they take more than one elementary step to complete. An intermediate is the reaction product of each of these steps, except for the last one, which forms the final product. Reactive intermediates are usually short lived and are very seldom isolated. Also, owing to the short lifetime, they do not remain in the product mixture.

Carbocation

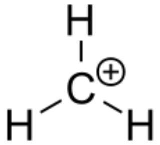
carbocation is an ion with a positively charged carbon atom. Among the simplest examples are the methenium CH_3^+, methanium CH_5^+ and vinyl $C_2H_3^+$ cations. A carbocation with a two-coordinate positive carbon derived from formal removal of a hydride ion (H^-) from an alkene is known as a *vinyl cation*. In the absence of geometric constraints, most substituted vinyl cations carry the formal positive charge on an sp-hydridized carbon atom of linear geometry. A two-coordinate approximately sp^2-hybridized cation resulting from the formal removal of a hydride ion from an arene is termed an *aryl cation*.



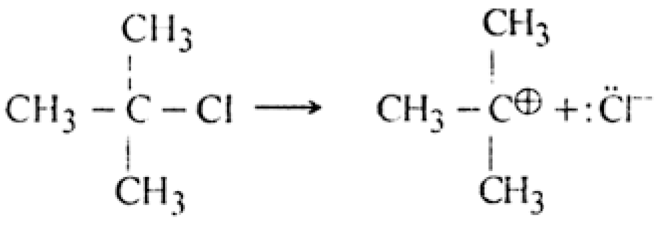
top view



side view



Generation of carbocation



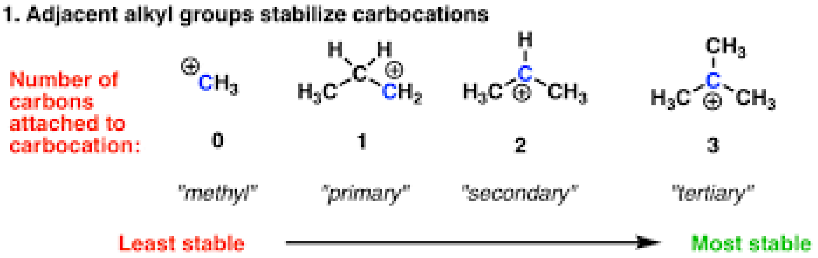
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} + :\ddot{Cl}^-$$

tert. butyl chloride

tert. butyl cation

Stability of carbocation

Alkyl-substituted carbocations follow the order 3° > 2° > 1° > methyl in stability, as can be inferred by the hydride ion affinity values (231, 246, 273, and 312 kcal/mol for $(CH_3)_3C^+$, $(CH_3)_2CH^+$, $CH_3CH^+_2$, and CH^+_3)

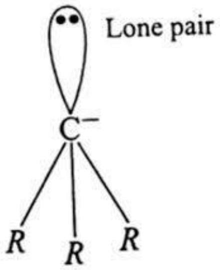


Carbanions

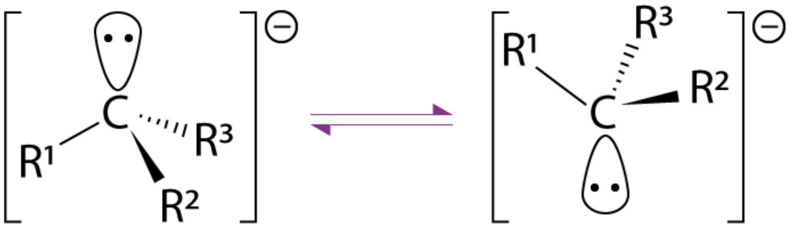
A carbanion is an anion in which carbon is trivalent (forms three bonds) and bears a formal negative charge. Formally, a carbanion is the conjugate base of a carbon acid:

$$R_3CH + :B^- \rightarrow R_3C:^- + HB$$

Absent π delocalization, the negative charge of a carbanion is localized in an spx hybridized orbital on carbon as a lone pair. As a consequence, localized alkyl, alkenyl/aryl, and alkynyl carbanions assume trigonal pyramidal, bent, and linear geometries, respectively. By Bent's rule, placement of the carbanionic lone pair electrons in an orbital with significant s character is favorable, accounting for the pyramidalized and bent geometries of alkyl and alkenyl carbanions, respectively. Valence shell electron pair repulsion (VSEPR) theory makes similar predictions. This contrasts with carbocations, which have a preference for unoccupied nonbonding orbitals of pure atomic p character, leading to planar and linear geometries, respectively, for alkyl and alkenyl carbocations.



Carbanions have a concentration of electron density at the negatively charged carbon, which, in most cases, reacts efficiently with a variety of electrophiles of varying strengths, including carbonyl groups, imines/iminium salts, halogenating reagents (e.g., N-bromosuccinimide and diiodine), and proton donors. A carbanion is one of several reactive intermediates in organic chemistry. In organic synthesis, organolithium reagents and Grignard reagents are commonly treated and referred to as "carbanions." This is a convenient approximation, although these species are generally clusters or complexes containing highly polar, but still covalent bonds metal–carbon bonds ($M\delta+–C\delta-$) rather than true carbanions.

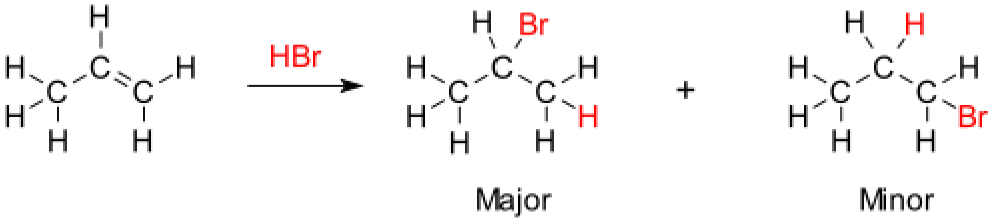


UNIT-II

HYDROCARBONS AND HALOGEN COMPOUNDS

Markovnikov's rule

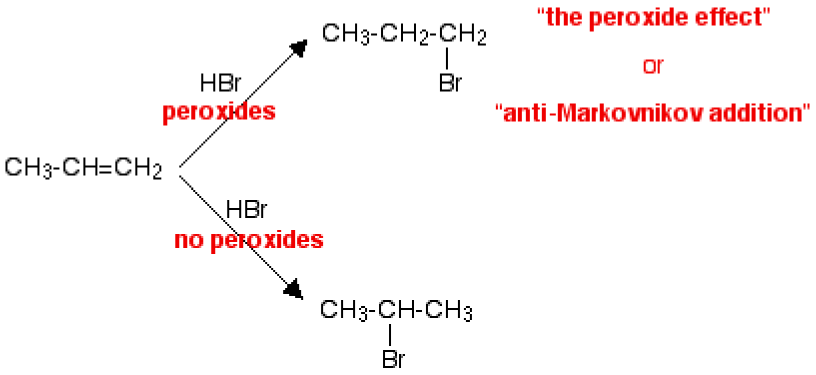
The rule states that with the addition of a protic acid HX or other polar reagent to an asymmetric alkene, the acid hydrogen (H) or electropositive part gets attached to the carbon with more hydrogen substituents, and the halide (X) group or electronegative part gets attached to the carbon with more alkyl substituents. This is in contrast to Markovnikov's original definition, in which the rule is stated that the X component is added to the carbon with the fewest hydrogen atoms while the hydrogen atom is added to the carbon with the greatest number of hydrogen atoms. The same is true when an alkene reacts with water in an addition reaction to form an alcohol which involve formation of carbocations. The hydroxyl group (OH) bonds to the carbon that has the greater number of carbon–carbon bonds, while the hydrogen bonds to the carbon on the other end of the double bond, that has more carbon–hydrogen bonds. Markovnikov's rule is illustrated by the reaction of propene with hydrobromic acid.



The chemical basis for Markovnikov's Rule is the formation of the most stable carbocation during the addition process. The addition of the hydrogen ion to one carbon atom in the alkene creates a positive charge on the other carbon, forming a carbocation intermediate. The more substituted the carbocation, the more stable it is, due to induction and hyperconjugation. The major product of the addition reaction will be the one formed from the more stable intermediate. Therefore, the major product of the addition of HBr (where Br is some atom more electronegative than H) to an alkene has the hydrogen atom in the less substituted position and Br in the more substituted position. But the other less substituted, less stable carbocation will still be formed at some concentration, and will proceed to be the minor product with the opposite, conjugate attachment of Br.

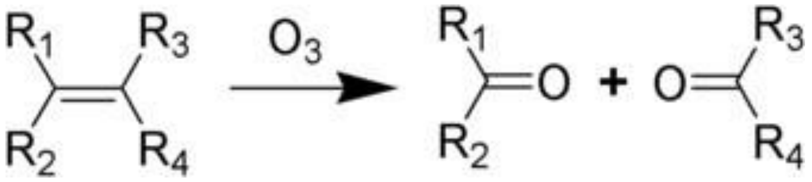
Peroxide effect

The change in regioselectivity of the addition of HBr to an alkene or alkyne in the presence of a peroxide. The regioselectivity for the addition reactions of other electrophiles such as HCl and H_3O^+ are not altered in the presence of a peroxide.

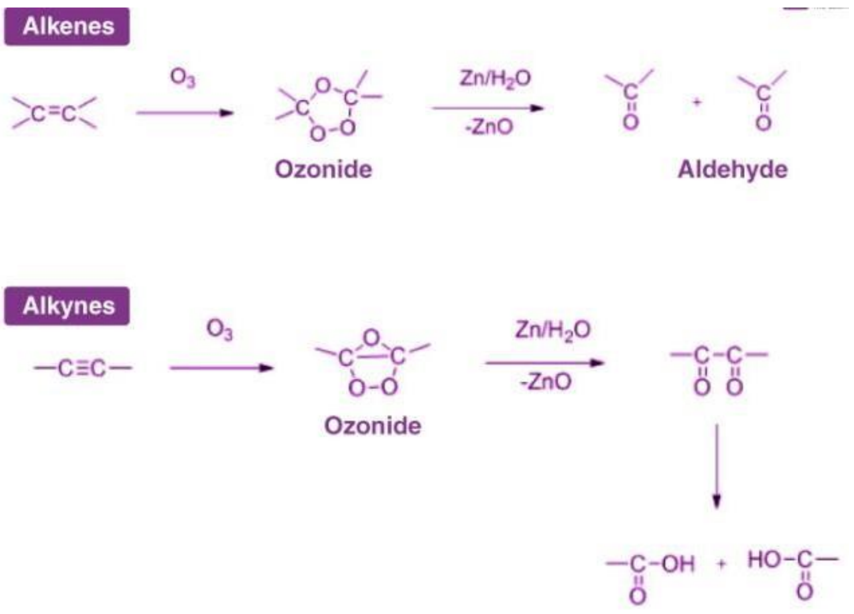


Ozonolysis

Ozonolysis is an organic reaction where the unsaturated bonds of alkenes, alkynes, or azo compounds are cleaved with ozone. Alkenes and alkynes form organic compounds in which the multiple carbon–carbon bond has been replaced by a carbonyl groupwhile azo compounds form nitrosamines. The outcome of the reaction depends on the type of multiple bond being oxidized and the work-up conditions.

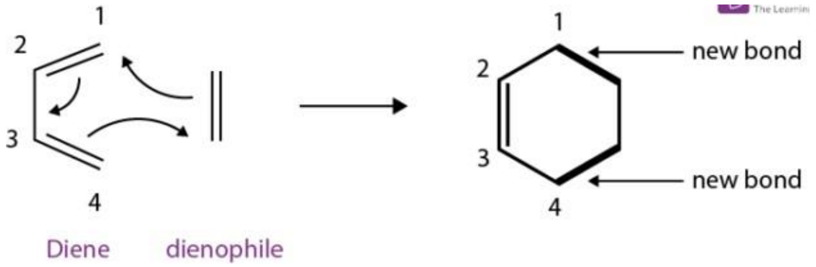


Alkenes can be oxidized with ozone to form alcohols, aldehydes or ketones, or carboxylic acids. In a typical procedure, ozone is bubbled through a solution of the alkene in methanol at −78 °C until the solution takes on a characteristic blue color, which is due to unreacted ozone. This indicates complete consumption of the alkene. Alternatively, various other chemicals can be used as indicators of this endpoint by detecting the presence of ozone.

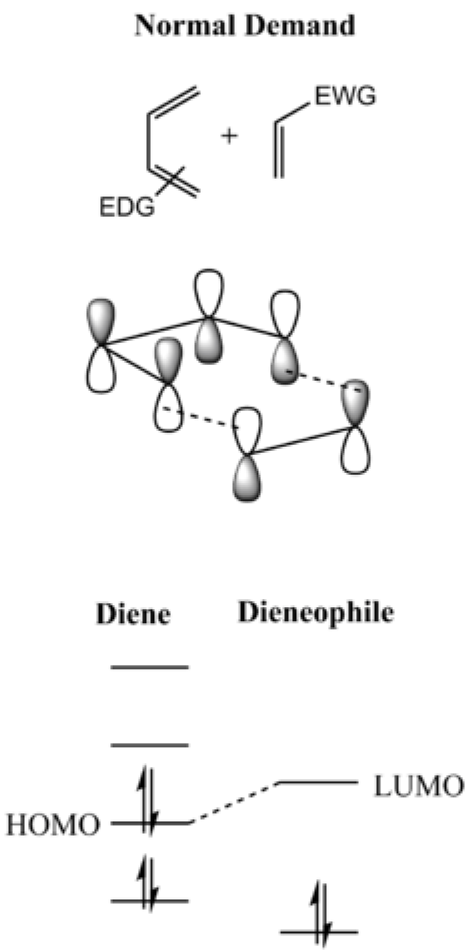


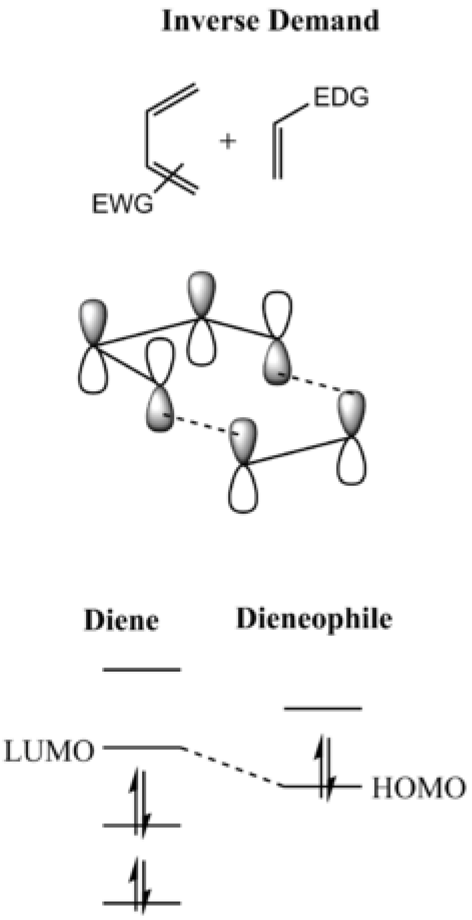
Diels–Alder reaction

The Diels–Alder reaction is the reaction between a conjugated diene and an alkene (dienophile) to form unsaturated six-membered rings. Since the reaction involves the formation of a cyclic product via a cyclic transition state, it is also referred to as a "cycloaddition". The Diels–Alder reaction is an electrocyclic reaction, which involves [4+2]-cycloaddition of 4 π-electrons of the conjugated diene and 2 π-electrons of the dienophile (an alkene or alkyne). The reaction involves the formation of new σ-bonds, which are energetically more stable than the π-bonds. This reaction has great synthetic importance and was discovered by two German chemists, Otto Diels and Kurt Alder in 1928. They were awarded the Nobel Prize in 1950.



A consideration of the reactants' frontier molecular orbitals (FMO) makes plain why this is so. For the more common "normal" electron demand Diels–Alder reaction, the more important of the two HOMO/LUMO interactions is that between the electron-rich diene's ψ^2 as the highest occupied molecular orbital (HOMO) with the electron-deficient dienophile's π* as the lowest unoccupied molecular orbital (LUMO)

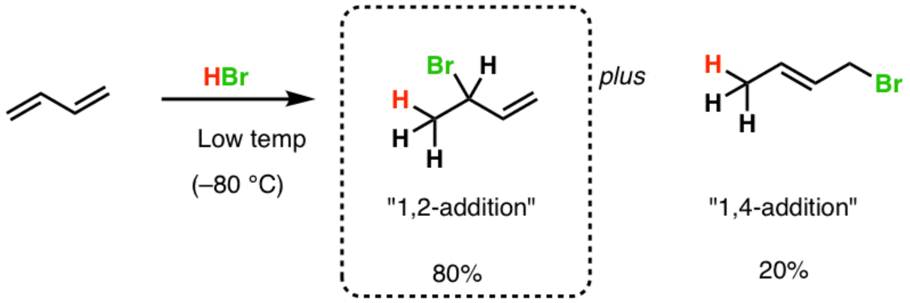




1, 2 and 1, 4 addition reaction

Both isolated and conjugated dienes undergo electrophilic addition reactions. In the case of isolated dienes, the reaction proceeds in a manner identical to alkene electrophilic addition. The addition of hydrogen bromide to 1,4-pentadiene leads to two products.

Low temperature addition of HBr to butadiene: 1,2 addition dominates

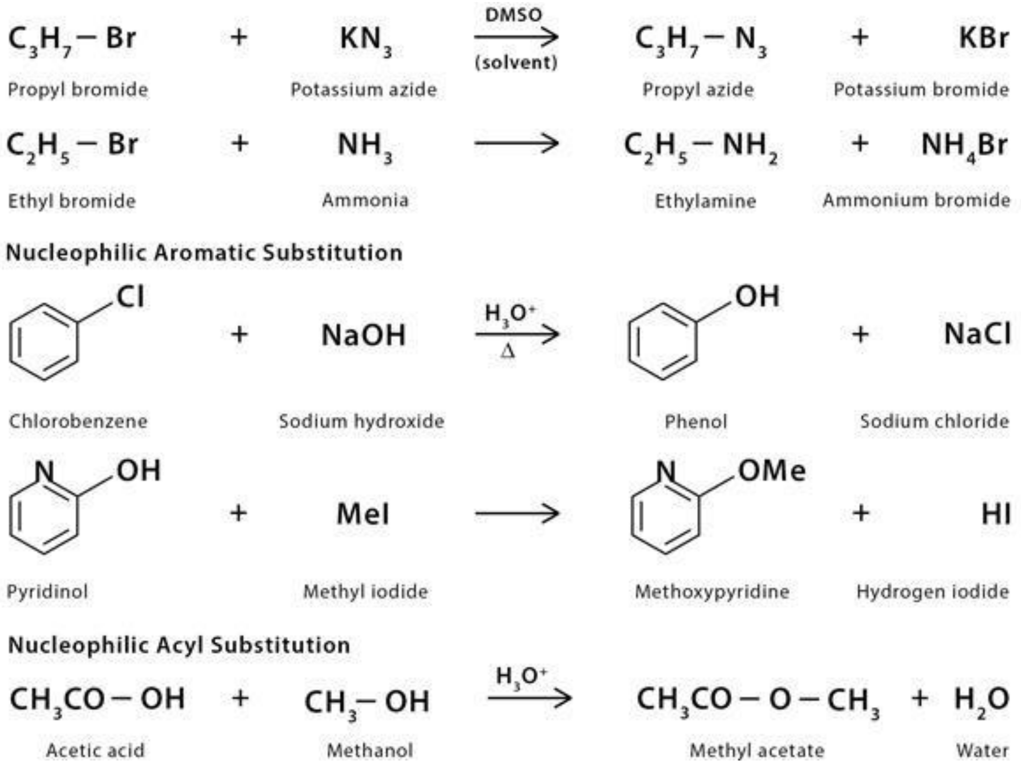


Types of reactions

Organic reactions are chemical reactions involving organic compounds. The basic organic chemistry reaction types are addition reactions, elimination reactions, substitution reactions, pericyclic reactions, rearrangement reactions, photochemical reactions and redox reactions. In organic synthesis, organic reactions are used in the construction of new organic molecule.

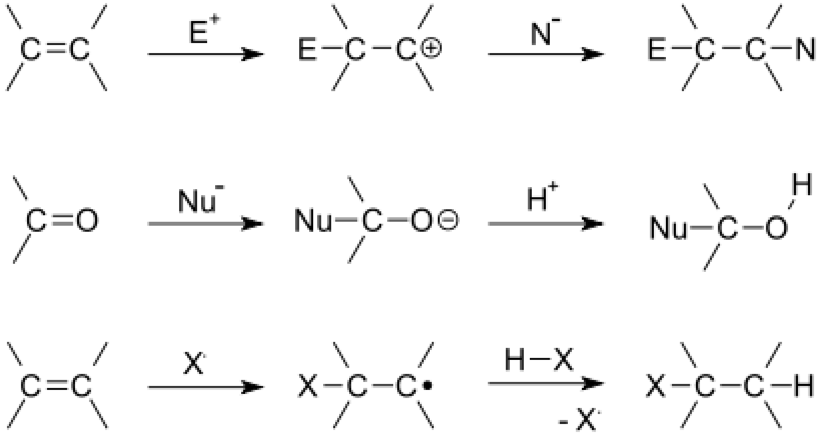
Substitution reaction

A substitution is a chemical reaction during which one functional group in a chemical compound is replaced by another functional group. Substitution reactions are of prime importance in organic chemistry. Nucleophiles, typically, have a lone pair of electrons in them. As the name suggests, they are attracted to the nucleus of an atom. Nucleophilic substitution is a substitution reaction in which an electron-rich nucleophile displaces the halogen atom bonded to the central carbon of an alkyl halide molecule. The halide ion that is displaced from the carbon atom is called the leaving group. Nucleophilic substitution reaction takes place at the site of a saturated carbon atom of aromatic, aliphatic, and acyl (RCO) compounds.

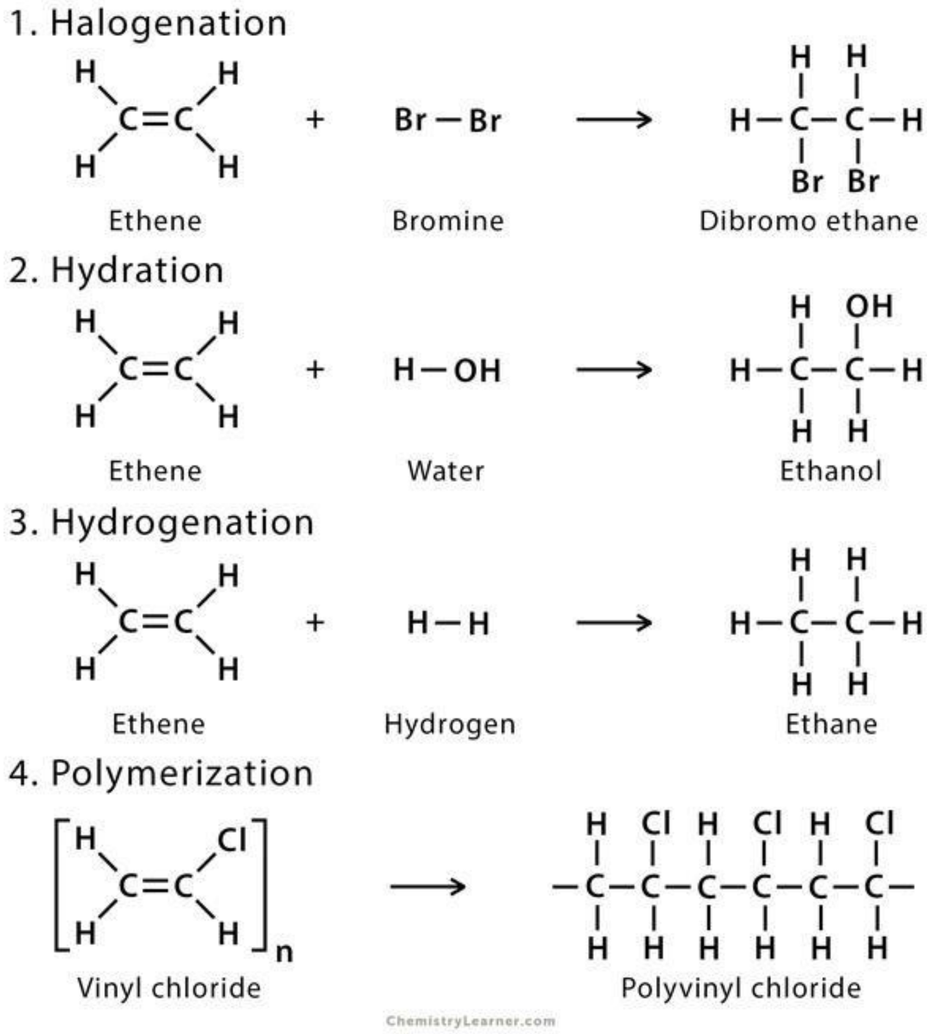


Addition reaction

In organic chemistry, an addition reaction is an organic reaction in which two or more molecules combine to generate a bigger one (the adduct). Molecules with carbon—hetero double bonds, such as carbonyl (C=O) or imine (C=N) groups, can be added because they have double-bond character as well.

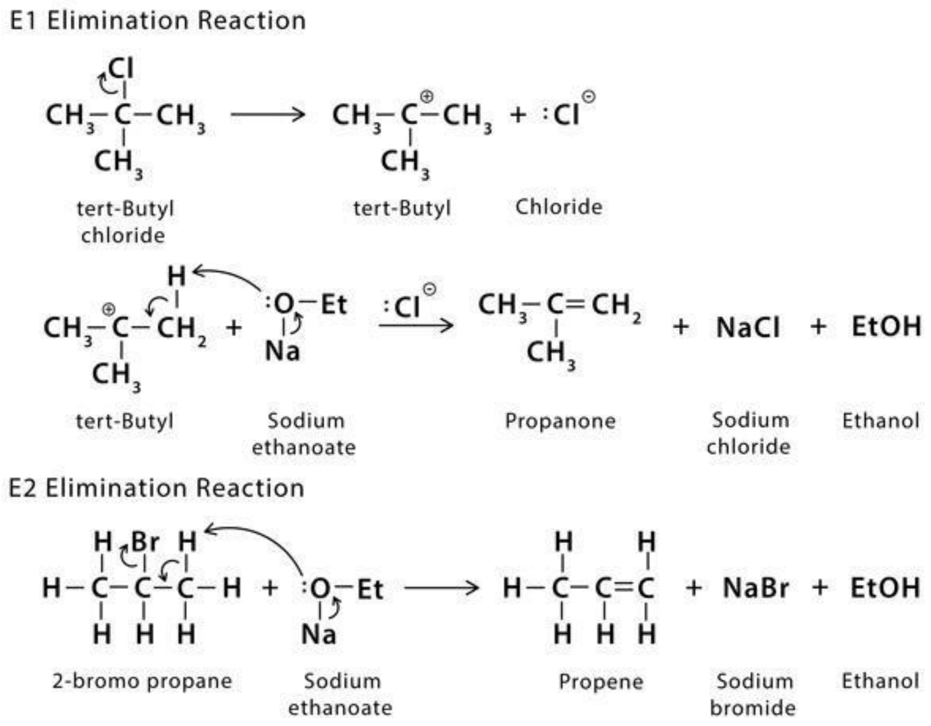


An addition reaction is the reverse of an elimination reaction. For instance, the hydration of an alkene to an alcohol is reversed by dehydration. There are two main types of polar addition reactions: electrophilic addition and nucleophilic addition. Two non-polar addition reactions exist as well, called free-radical addition and cycloadditions. Addition reactions are also encountered in polymerizations and called addition polymerization.



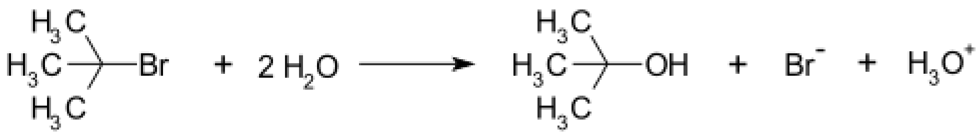
Elimination reaction

An elimination reaction is a type of organic reaction in which two substituents are removed from a molecule in either a one- or two-step mechanism.The one-step mechanism is known as the E2 reaction, and the two-step mechanism is known as the E1 reaction. The numbers refer not to the number of steps in the mechanism, but rather to the kinetics of the reaction: E2 is bimolecular while E1 is unimolecular (first-order). In cases where the molecule is able to stabilize an anion but possesses a poor leaving group, a third type of reaction, E1CB, exists. Finally, the pyrolysis of xanthate and acetate esters proceed through an "internal" elimination mechanism, the Ei mechanism.



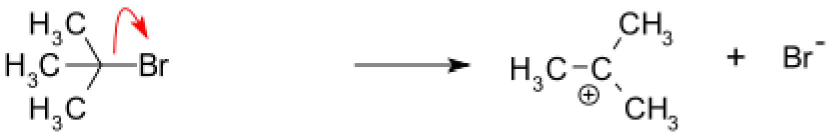
SN1 reaction

The SN1 reaction is a substitution reaction in organic chemistry, the name of which refers to the Hughes-Ingold symbol of the mechanism. "SN" stands for "nucleophilic substitution", and the "1" says that the rate-determining step is unimolecular. Thus, the rate equation is often shown as having first-order dependence on electrophile and zero-order dependence on nucleophile. This relationship holds for situations where the amount of nucleophile is much greater than that of the intermediate. Instead, the rate equation may be more accurately described using steady-state kinetics. The reaction involves a carbocation intermediate and is commonly seen in reactions of secondary or tertiary alkyl halides under strongly basic conditions or, under strongly acidic conditions, with secondary or tertiary alcohols. With primary and secondary alkyl halides, the alternative SN2 reaction occurs. An example of a reaction taking place with an SN1 reaction mechanism is the hydrolysis of tert-butyl bromide forming tert-butanol.

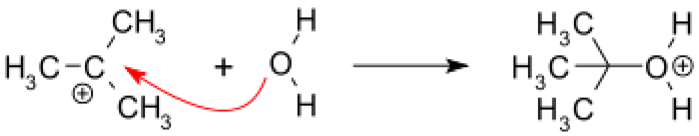


This SN1 reaction takes place in three steps:

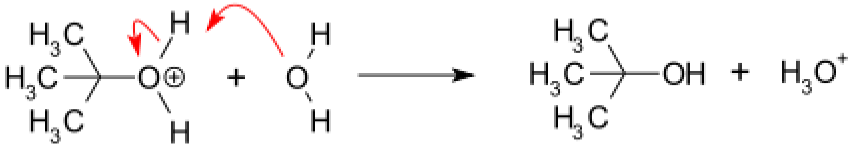
- Formation of a tert-butyl carbocation by separation of a leaving group (a bromide anion) from the carbon atom: this step is slow.



- Nucleophilic attack: the carbocation reacts with the nucleophile. If the nucleophile is a neutral molecule (i.e. a solvent) a third step is required to complete the reaction. When the solvent is water, the intermediate is an oxonium ion. This reaction step is fast.

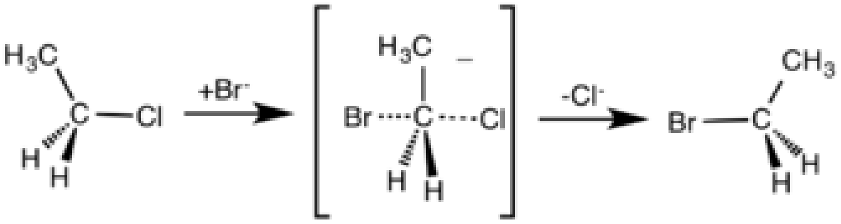


- Deprotonation: Removal of a proton on the protonated nucleophile by water acting as a base forming the alcohol and a hydronium ion. This reaction step is fast.

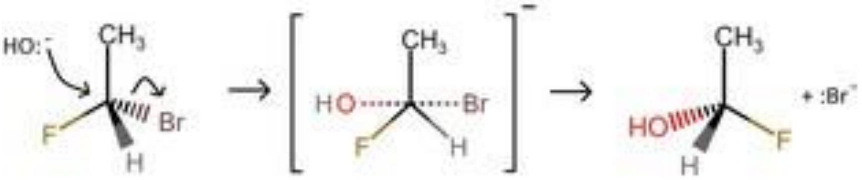


SN2 reaction

The SN2 reaction is a type of reaction mechanism that is common in organic chemistry. In this mechanism, one bond is broken and one bond is formed synchronously, i.e., in one step. SN2 is a kind of nucleophilic substitution reaction mechanism, the name referring to the Hughes-Ingold symbol of the mechanism. Since two reacting species are involved in the slow step, this leads to the term substitution nucleophilic or SN2; the other major kind is SN1. Many other more specialized mechanisms describe substitution reactions. The reaction type is so common that is it has other names, e.g. "bimolecular nucleophilic substitution", or, among inorganic chemists, "associative substitution" or "interchange mechanism". In an example of the SN2 reaction, the attack of Br− (the nucleophile) on an ethyl chloride (the electrophile) results in ethyl bromide, with chloride ejected as the leaving group.



If the molecule that is undergoing SN2 reaction has a chiral centre, then it is possible that the optical activity of the product would be different from that of the reactant. In an example, 1-bromo-1-fluoroethane can undergo SN2 reaction to form 1-fluoroethan-1-ol, with the nucleophile being an OH- group. In this case, if the reactant is levorotatory, then the product would be dextrorotatory, and vice versa.



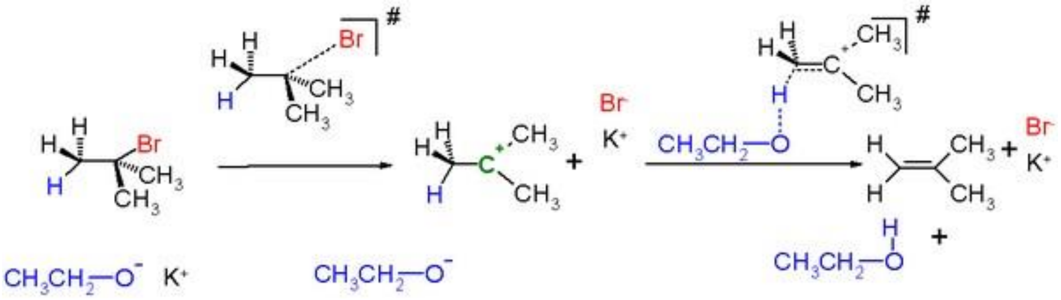
SN2 attack occurs if the backside route of attack is not sterically hindered by substituents on the substrate (ethyl chloride being the substrate above). Therefore, this mechanism usually occurs at unhindered primary and secondary carbon centres. If there is steric crowding on the substrate near the leaving group, such as at a tertiary carbon centre, the substitution will involve an SN1 rather than an SN2 mechanism.

E1 mechanism

E1 is a model to explain a particular type of chemical elimination reaction. E1 stands for unimolecular elimination and has the following specifications. It is a two-step process of elimination: ionization and deprotonation. Ionization: the carbon-halogen bond breaks to give a carbocation intermediate. deprotonation of the carbocation.

- E1 typically takes place with tertiary alkyl halides, but is possible with some secondary alkyl halides.
- The reaction rate is influenced only by the concentration of the alkyl halide because carbocation formation is the slowest step, as known as the rate-determining step. Therefore, first-order kinetics apply.
- The reaction usually occurs in the complete absence of a base or the presence of only a weak base.
- E1 reactions are in competition with SN1 reactions because they share a common carbocationic intermediate.
- A secondary deuterium isotope effect of slightly larger than 1 is observed.

- There is no antiperiplanar requirement. An example is the pyrolysis of a certain sulfonate ester of menthol.

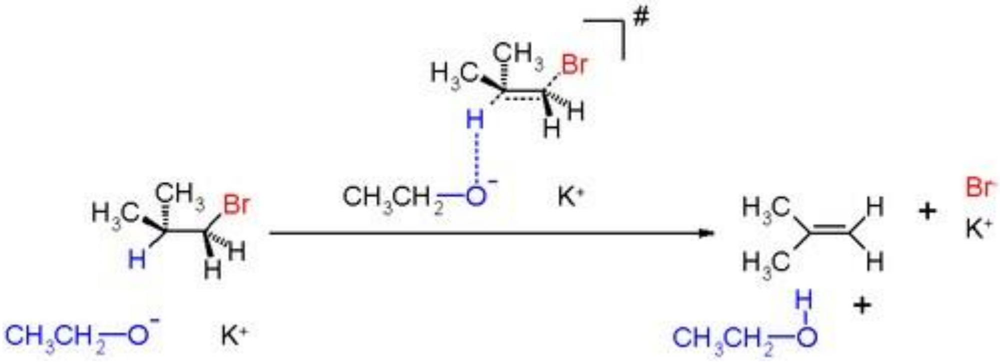


E2 mechanism

The E2 mechanism, where E2 stands for bimolecular elimination involves a one-step mechanism in which carbon-hydrogen and carbon-halogen bonds break to form a double bond (C=C Pi bond).The specifics of the reaction are as follows

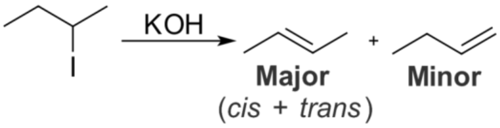
- E2 is single step elimination, with a single transition state.
- It is typically undergone by primary substituted alkyl halides, but is possible with some secondary alkyl halides and other compounds.
- The reaction rate is second order, because it's influenced by both the alkyl halide and the base.
- Because the E2 mechanism results in the formation of a pi bond, the two leaving groups need to be antiperiplanar. An antiperiplanar transition state has staggered conformation with lower energy than a synperiplanar transition state which is in eclipsed conformation with higher energy. The reaction mechanism involving staggered conformation is more favorable for E2 reactions.
- E2 typically uses a strong base. It must be strong enough to remove weakly acidic hydrogen.
- In order for the pi bond to be created, the hybridization of carbons needs to be lowered from sp^3 to sp^2.
- The C-H bond is weakened in the rate determining step and therefore a primary deuterium isotope effect much larger than 1 is observed.
- E2 competes with the SN2 reaction mechanism if the base can also act as a nucleophile.

An example of this type of reaction in scheme 1 is the reaction of isobutylbromide with potassium ethoxide in ethanol. The reaction products are isobutene, ethanol and potassium bromide.



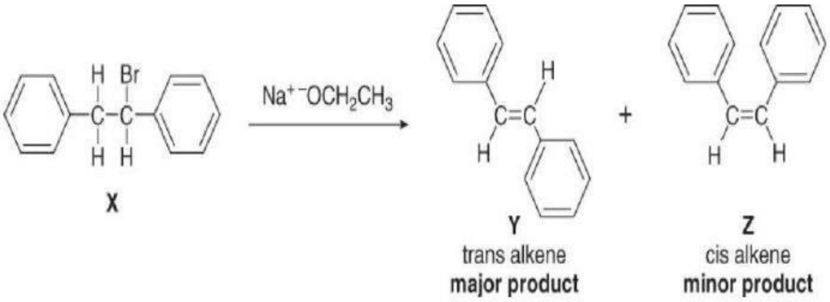
Hofmann rule

Hofmann elimination is an elimination reaction of an amine. The least stable alkene, called the Hofmann product, is formed. This tendency, known as the Hofmann alkene synthesis rule, is in contrast to usual elimination reactions, where Zaitsev's rule predicts the formation of the most stable alkene.



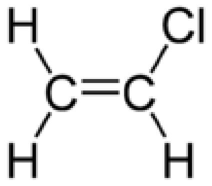
Saytzeff rule

Saytzeff Rule implies that base-induced eliminations (E2) will lead predominantly to the olefin in which the double bond is more highly substituted, i.e. that the product distribution will be controlled by thermodynamics.



Preparation, properties and uses of vinyl chloride

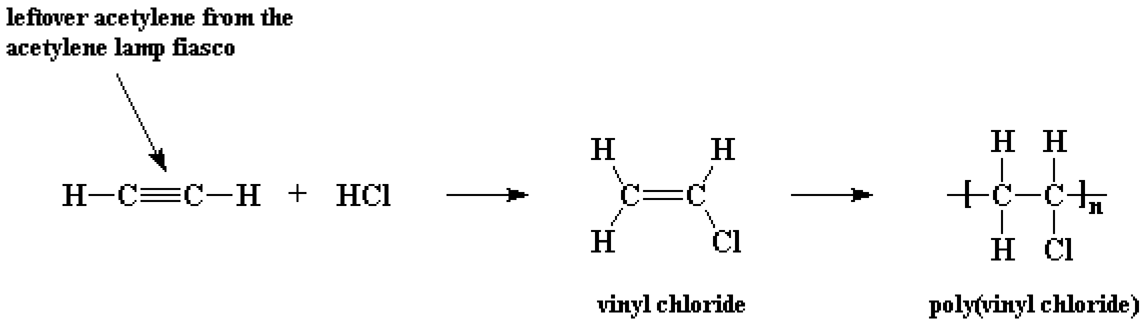
Vinyl chloride is an organochloride with the formula H2C=CHCl that is also called vinyl chloride monomer (VCM) or chloroethene. This colorless compound is an important industrial chemical chiefly used to produce the polymer polyvinyl chloride (PVC).



Vinyl chloride is a gas with a sweet odor. It is highly toxic, flammable, and carcinogenic. It can be formed in the environment when soil organisms break down chlorinated solvents. Vinyl chloride that is released by industries or formed by the breakdown of other chlorinated chemicals can enter the air and drinking water supplies.

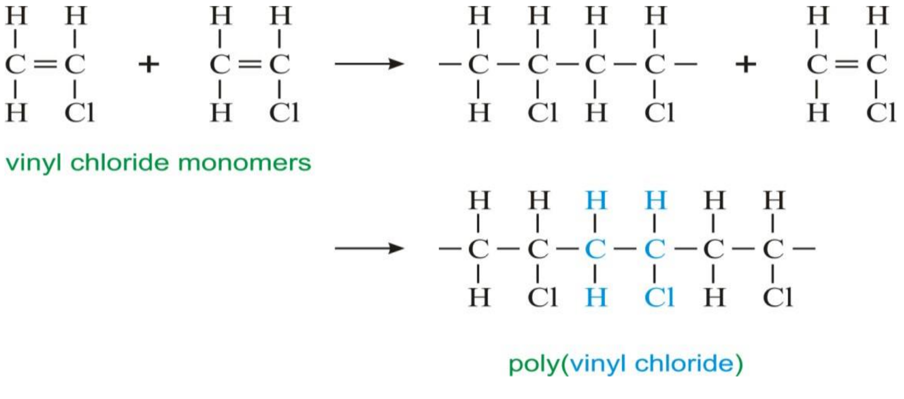
Preparation of vinyl chloride

PVC was one of those odd discoveries that actually had to be made twice. It seems around a hundred years ago, a few German entrepreneurs decided they were going to make loads of cash lighting people's homes with lamps fueled by acetylene gas. Wouldn't you know it, right about the time they had produced tons of acetylene to sell to everyone who was going to buy their lamps, new efficient electric generators were developed which made the price of electric lighting drop so low that the acetylene lamp business was finished. That left a lot of acetylene laying around.



Properties of vinyl chloride

Polymerization is a reaction of connecting many monomers in one long molecule whereby polymers are created.

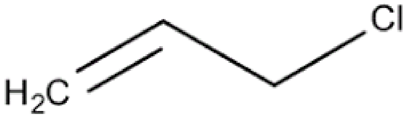


2.13.4 Uses of vinyl chloride

Vinyl chloride is used primarily to make polyvinyl chloride (PVC); PVC is used to make a variety of plastic products, including pipes, wire and cable coatings, and packaging materials. Vinyl chloride is also produced as a combustion product in tobacco smoke.

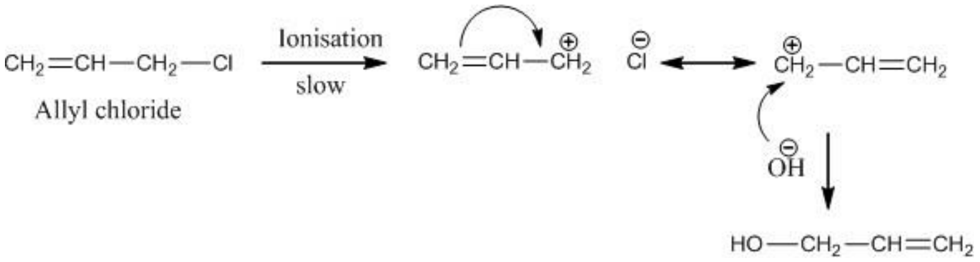
Preparation, properties and uses of allyl chloride

Allyl chloride is the organic compound with the formula $CH_2=CHCH_2Cl$. This colorless liquid is insoluble in water but soluble in common organic solvents. It is mainly converted to epichlorohydrin, used in the production of plastics. It is a chlorinated derivative of propylene. It is an alkylating agent, which makes it both useful and hazardous to handle.



Allyl chloride is produced by the chlorination of propylene. At lower temperatures, the main product is 1,2-dichloropropane, but at 500 °C, allyl chloride predominates, being formed via a free radical reaction.

$$CH_3CH=CH_2 + Cl_2 \rightarrow ClCH_2CH=CH_2 + HCl$$



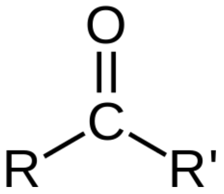
The great majority of allyl chloride is converted to epichlorohydrin. Other commercially significant derivatives include allyl alcohol, allylamine, allyl isothiocyanate and 1-bromo-3-chloropropane. As an alkylating agent, it is useful in the manufacture of pharmaceuticals and pesticides, such as mustard oil.

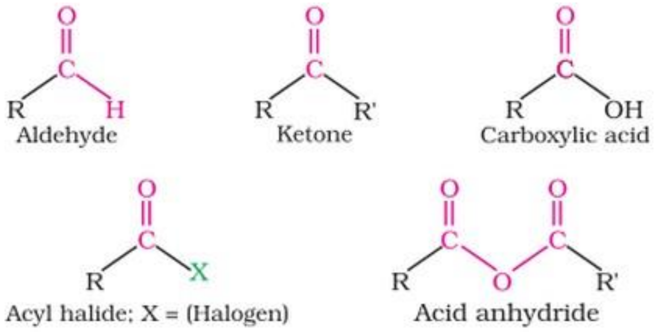
UNIT-III

CARBONYL COMPOUNDS AND CARBOXYLIC ACID

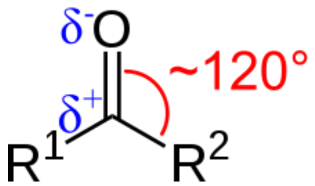
Carbonyl compounds

In organic chemistry, a carbonyl group is a functional group composed of a carbon atom double-bonded to an oxygen atom: C=O. It is common to several classes of organic compounds, as part of many larger functional groups. A compound containing a carbonyl group is often referred to as a carbonyl compound.





For organic compounds, the length of the C-O bond does not vary widely from 120 picometers. Inorganic carbonyls have shorter C-O distances: CO, 113; CO_2, 116; and $COCl_2$, 116 pm. The carbonyl carbon is typically electrophilic. A qualitative order of electrophilicity is RCHO (aldehydes) > R_2CO (ketones) > RCO_2R' (esters) > $RCONH_2$ (amides). A variety of nucleophiles attack, breaking the carbon-oxygen double bond.

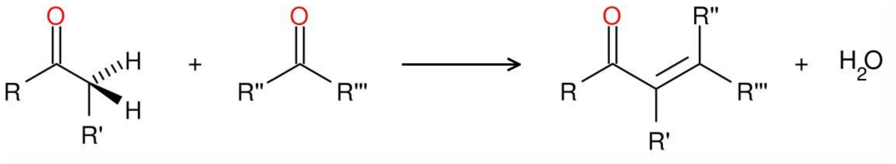


Infrared spectroscopy: the C=O double bond absorbs infrared light at wavenumbers between approximately 1600–1900 cm^{-1}(5263 nm to 6250 nm). The exact location of the absorption is well understood with respect to the geometry of the molecule. This absorption is known as the "carbonyl stretch" when displayed on an infrared absorption spectrum. In addition, the ultraviolet-visible spectra of propanone in water gives an absorption of carbonyl at 257 nm.

Nuclear magnetic resonance: the C=O double-bond exhibits different resonances depending on surrounding atoms, generally a downfield shift. The ^{13}C NMR of a carbonyl carbon is in the range of 160–220 ppm.

Aldol condensation

An aldol condensation is a condensation reaction in organic chemistry in which an enol or an enolate ion reacts with a carbonyl compound to form a β-hydroxyaldehyde or β-hydroxyketone (an aldol reaction), followed by dehydration to give a conjugated enone.

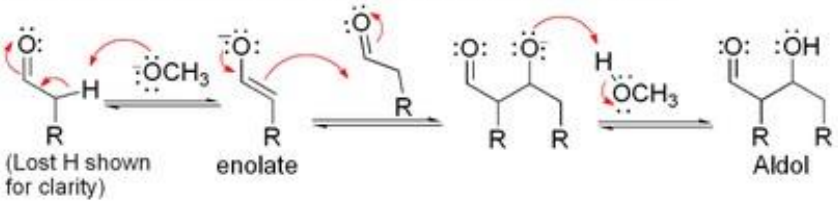


Aldol condensations are important in organic synthesis and biochemistry as ways to form carbon–carbon bonds.In its usual form, it involves the nucleophilic addition of a ketone enolate to an aldehyde to form a β-hydroxy ketone, or "aldol" (aldehyde + alcohol), a structural unit found in many naturally occurring molecules and pharmaceuticals.

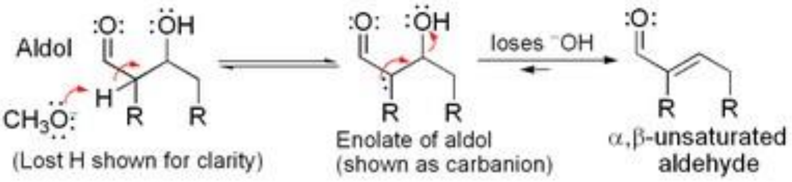
Mechanism

The first part of this reaction is an aldol reaction, the second part a dehydration an elimination reaction. Dehydration may be accompanied by decarboxylation when an activated carboxyl group is present. The aldol addition product can be dehydrated via two mechanisms; a strong base like potassium t-butoxide, potassium hydroxide or sodium hydride deprotonates the product to an enolate, which eliminates via the E_1cB mechanism, while dehydration in acid proceeds via an E_1 reaction mechanism. Depending on the nature of the desired product, the aldol condensation may be carried out fewer than two broad types of conditions: kinetic control or thermodynamic control.

Base catalyzed aldol reaction (shown using $^{-}OCH_3$ as base)



Base catalyzed dehydration (sometimes written as a single step)

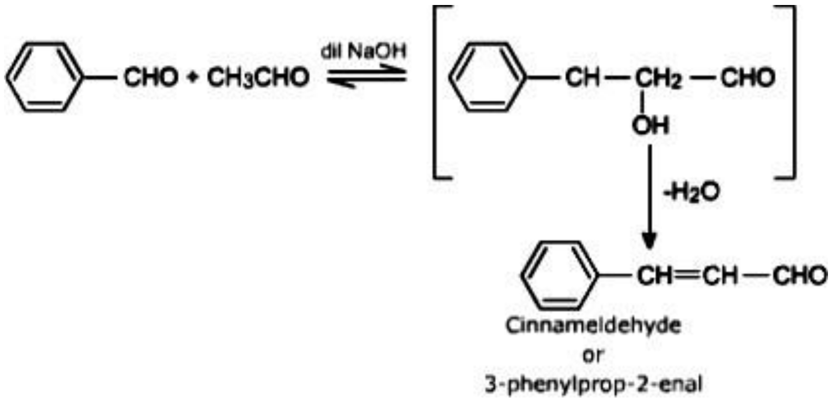


Crossed aldol condensation

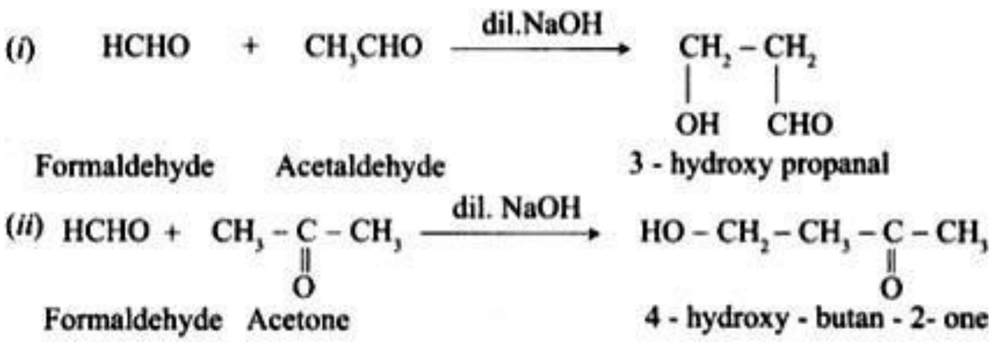
A crossed aldol condensation is a result of two dissimilar carbonyl compounds containing α-hydrogen(s) undergoing aldol condensation. Ordinarily, this leads to four possible products as either carbonyl compound can act as the nucleophile and self-condensation is possible, which makes a synthetically useless mixture. However, this problem can be avoided if one of the compounds does not contain an α-hydrogen, rendering it non-enolizable.

In an aldol condensation between an aldehyde and a ketone, the ketone acts as the nucleophile, as its carbonyl carbon does not possess high electrophilic character due to the +I effect and steric hindrance. Usually, the crossed product is the major one. Any traces of the self-aldol product from the aldehyde may be disallowed by first preparing a mixture of a suitable base and the ketone and then adding the aldehyde slowly to the said reaction mixture. Using too concentrated base could lead to a competing Cannizzaro reaction.

When aldol condensation is carried out between two different aldehydes and/ or ketones, a mixture of self and cross-aldol products are obtained.

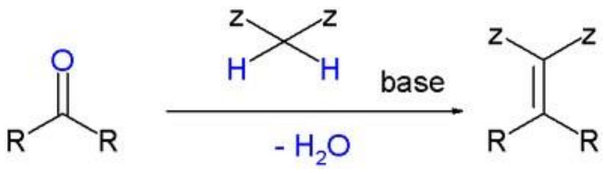


Aldol condensation can takes place between two different aldehyde or ketones or between one aldehyde and one ketone is called crossed or mixed aldol condensation.

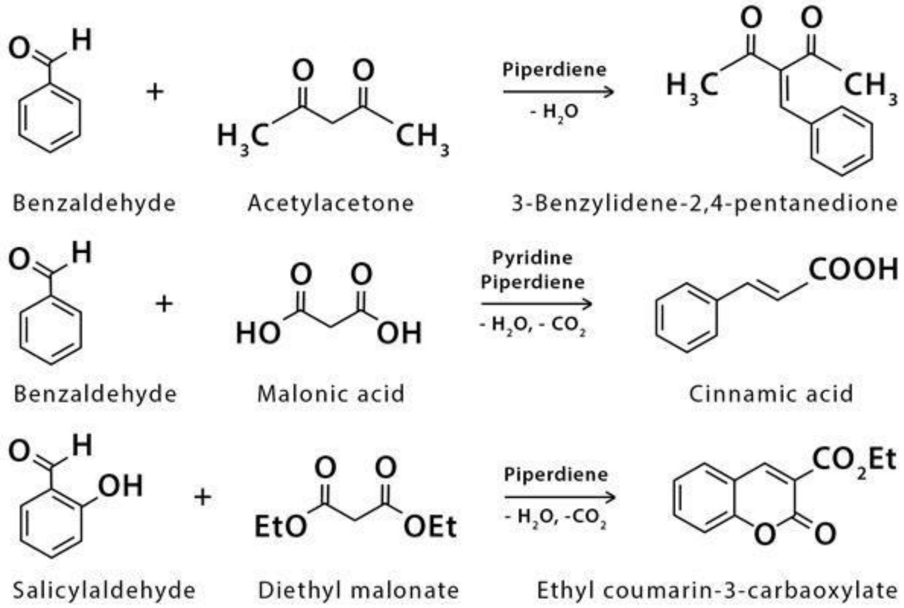


Knoevenagel reaction

The Knoevenagel condensation reaction is an organic reaction named after Emil Knoevenagel. It is a modification of the aldol condensation. A Knoevenagel condensation is a nucleophilic addition of an active hydrogen compound to a carbonyl group followed by a dehydration reaction in which a molecule of water is eliminated. The product is often an α,β-unsaturated ketone. In this reaction the carbonyl group is an aldehyde or a ketone. The catalyst is usually a weakly basic amine. The active hydrogen component has the form.

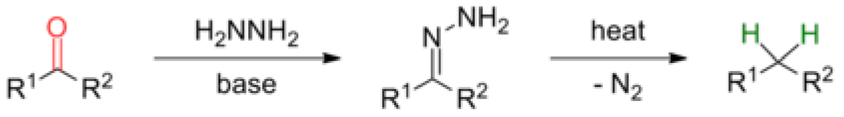


Knoevenagel condensation is used in the synthesis of cinnamic acid and coumarin.

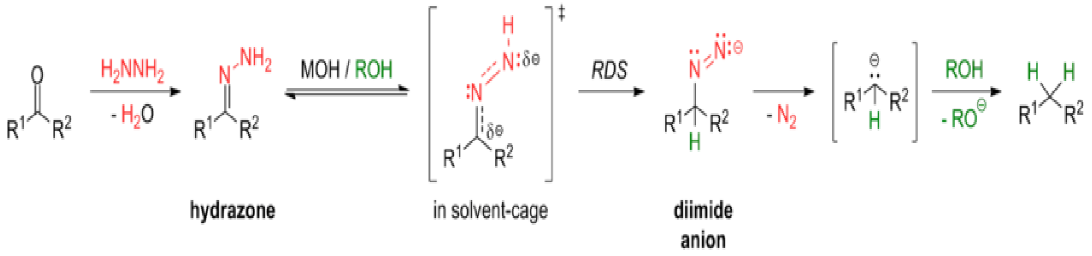


Wolff–Kishner reaction

The Wolff–Kishner reduction is a reaction used in organic chemistry to convert carbonyl functionalities into methylene groups. In the context of complex molecule synthesis, it is most frequently employed to remove a carbonyl group after it has served its synthetic purpose of activating an intermediate in a preceding step.

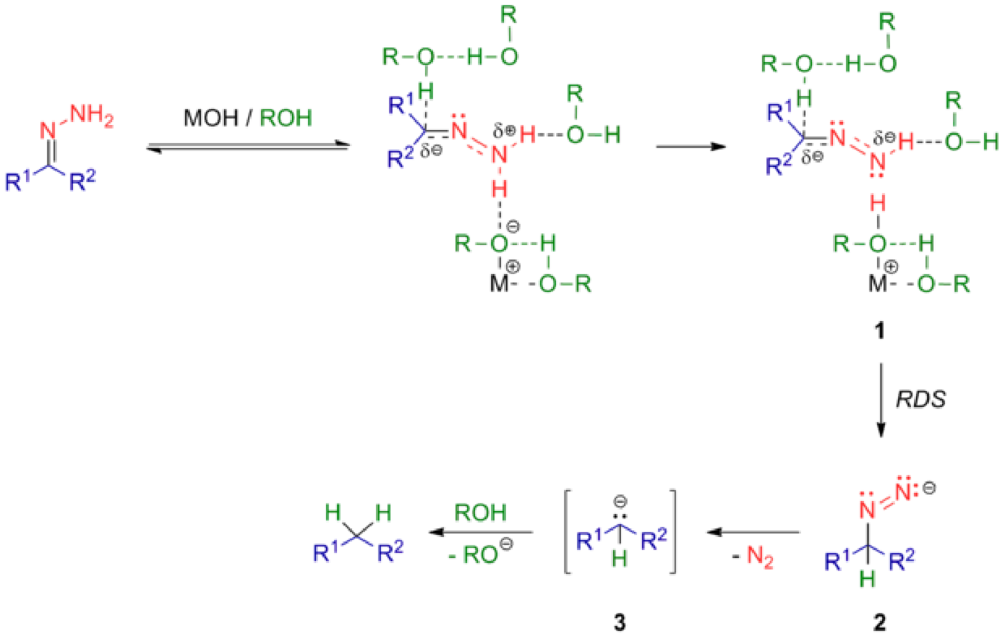


In general, the reaction mechanism first involves the in situ generation of a hydrazone by condensation of hydrazine with the ketone or aldehyde substrate. Sometimes it is however advantageous to use a pre-formed hydrazone as substrate. The rate determining step of the reaction is de-protonation of the hydrazone by an alkoxide base to form a diimide anion by a concerted, solvent mediated protonation/de-protonation step.



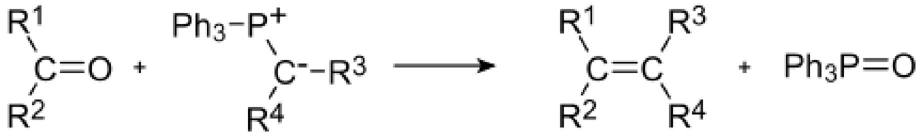
Mechanism

The rate of the reaction depends on the concentration of the hydroxylic solvent and on the cation in the alkoxide catalyst. The presence of crown ether in the reaction medium can increase the reactivity of the hydrazone anion 1 by dissociating the ion pair and therefore enhance the reaction rate. The final step of the Wolff–Kishner reduction is the collapse of the diimide anion 2 in the presence of a proton source to give the hydrocarbon via loss of dinitrogen to afford an alkyl anion 3, which undergoes rapid and irreversible acid-base reaction with solvent to give the alkane.



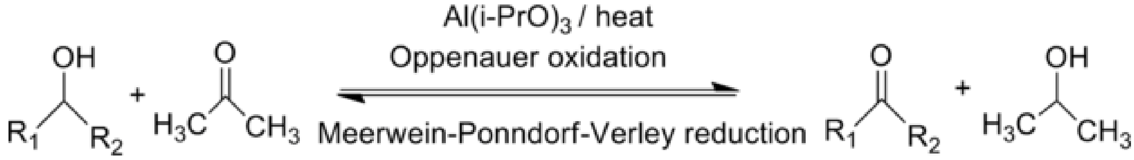
Wittig reaction

The Wittig reaction or Wittig olefination is a chemical reaction of an aldehyde or ketone with a triphenyl phosphonium ylide called a Wittig reagent. Wittig reactions are most commonly used to convert aldehydes and ketones to alkenes. Most often, the Wittig reaction is used to introduce a methylene group using methylenetriphenylphosphorane ($Ph_3P=CH_2$). Using this reagent, even a sterically hindered ketone such as camphor can be converted to its methylene derivative.



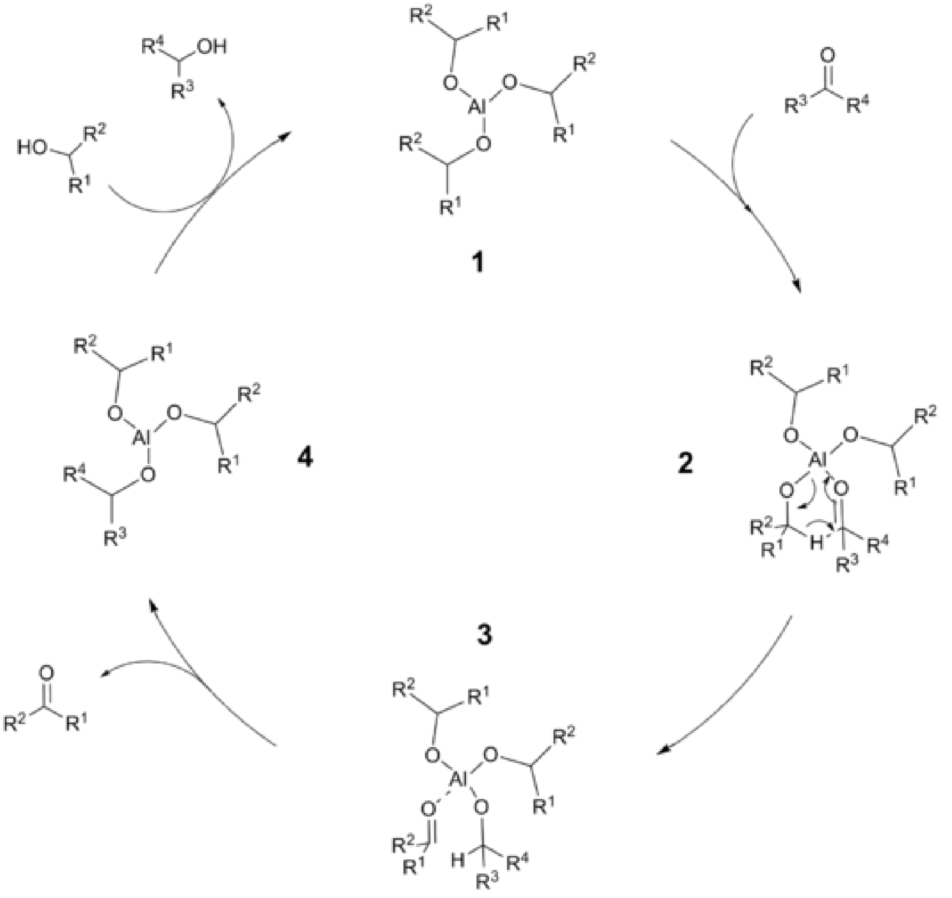
Meerwein–Ponndorf–Verley (MPV) reduction

The Meerwein–Ponndorf–Verley (MPV) reduction in organic chemistry is the reduction of ketones and aldehydes to their corresponding alcohols utilizing aluminium alkoxide catalysis in the presence of a sacrificial alcohol.The advantages of the MPV reduction lie in its high chemoselectivity, and its use of a cheap environmentally friendly metal catalyst. The MPV reduction was discovered by Meerwein and Schmidt, and separately by Verley in 1925. They found that a mixture of aluminium ethoxide and ethanol could reduce aldehydes to their alcohols. Ponndorf applied the reaction to ketones and upgraded the catalyst to aluminium isopropoxide in isopropanol.



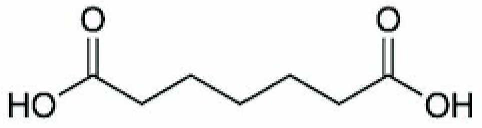
Mechanism

The MPV reduction is believed to go through a catalytic cycle involving a six-member ring transition state. Starting with the aluminium alkoxide 1, a carbonyl oxygen is coordinated to achieve the tetra coordinated aluminium intermediate 2. Between intermediates 2 and 3 the hydride is transferred to the carbonyl from the alkoxy ligand via a pericyclic mechanism. At this point the new carbonyl dissociates and gives the tricoordinated aluminium species 4. Finally, an alcohol from solution displaces the newly reduced carbonyl to regenerate the catalyst 1.



Dicarboxylic acid

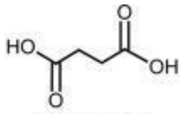
A dicarboxylic acid is an organic compound containing two carboxyl functional groups (−COOH). The general molecular formula for dicarboxylic acids can be written as $HO_2C-R-CO_2H$, where R can be aliphatic or aromatic. In general, dicarboxylic acids show similar chemical behavior and reactivity to monocarboxylic acids. Dicarboxylic acids are also used in the preparation of copolymers such as polyamides and polyesters. The most widely used dicarboxylic acid in the industry is adipic acid, which is a precursor used in the production of nylon. Other examples of dicarboxylic acids include aspartic acid and glutamic acid, two amino acids in the human body. The name can be abbreviated to diacid.

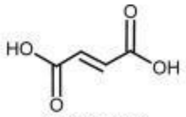


Properties

Dicarboxylic acids are crystalline solids. Solubility in water and melting point of the α,ω- compounds progress in a series as the carbon chains become longer with alternating between odd and even numbers of carbon atoms, so that for even numbers of carbon atoms the melting point is higher than for the next in the series with an odd number. These compounds are weak dibasic acids with pKa tending towards values of ca. 4.5 and 5.5 as the separation between the two carboxylate groups increases. Thus, in an aqueous solution at pH about 7, typical of biological systems, the Henderson–Hasselbalch equation indicates they exist predominantly as dicarboxylate anions.

Blanc's Rule says that heating a barium salt of a dicarboxylic acid, or dehydrating it with acetic anhydride will yield a cyclic acid anhydride if the carbon atoms bearing acid groups. So succinic acid will yield succinic anhydride. For acids with carboxylic groups at position 1 and 6 this dehydration causes loss of carbon dioxide and water to form a cyclic ketone, for example, adipic acid will form cyclopentanone.


Succinic acid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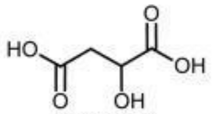
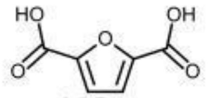
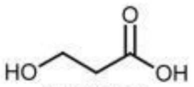
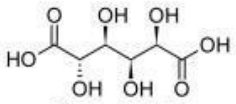
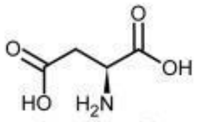
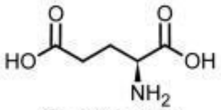

Malic acid

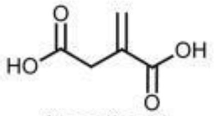

2,5-Furan
dicarboxylic acid

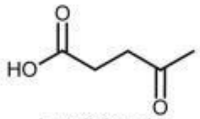

3-Hydroxy
propionic acid

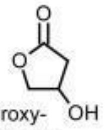

Glucaric acid

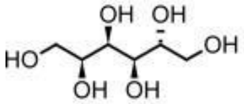

Aspartic acid

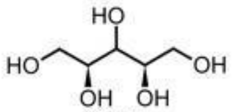

Glutamic acid

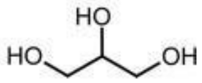

Itaconic acid


Levulinic acid


3-Hydroxy-
butyrolactone

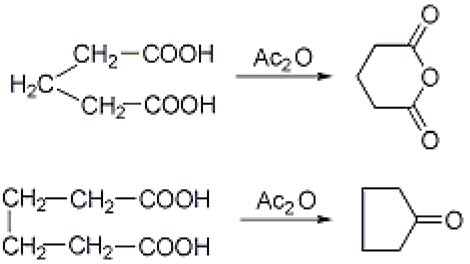

Sorbitol


Xylitol


Glycerol

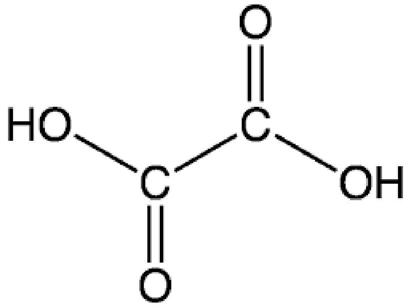
Blanc Rule

Cyclization of dicarboxylic acids on heating with acetic anhydride to give either cyclic anhydrides or ketones depending on the respective positions of the carboxyl groups; 1,4- and 1,5-diacids yield anhydrides, while diacids in which the carboxy groups are in 1,6 or further removed positions yield ketones.



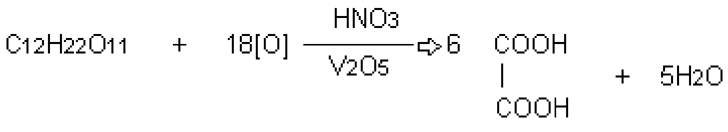
Preparation, proerties and uses of oxalic acid

Oxalic acid is an organic acid with the IUPAC name ethanedioic acid and formula $HO_2C{-}CO_2H$. It is the simplest dicarboxylic acid. It is a white crystalline solid that forms a colorless solution in water. Its name comes from the fact that early investigators isolated oxalic acid from flowering plants of the genus Oxalis, commonly known as wood-sorrels. It occurs naturally in many foods, but excessive ingestion of oxalic acid or prolonged skin contact can be dangerous. Oxalic acid has much greater acid strength than acetic acid. It is a reducing agent and its conjugate base, known as oxalate.



Preparation of oxalic acid

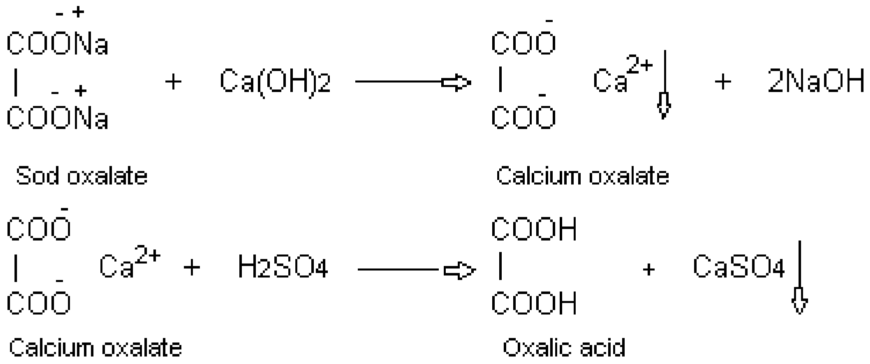
Oxalic acid is mainly manufactured by the oxidation of carbohydrates or glucose using nitric acid or air in the presence of vanadium pentoxide. A variety of precursors can be used including glycolic acid and ethylene glycol. A newer method entails oxidative carbonylation of alcohols to give the diesters of oxalic acid.



$$C_{12}H_{22}O_{11} + 18[O] \xrightarrow[V_2O_5]{HNO_3} 6\begin{array}{l}COOH\\ |\\ COOH\end{array} + 5H_2O$$

Oxalic Acid

The sodium oxalate thus formed is dissolved in water and calcium hydroxide added to precipitate calcium oxalate. The solution is filtered and the filtrate treated with the calculated quantity of dilute sulphuric acid to liberate the oxalic acid. Calcium sulphate precipitates, and oxalic acid is crystallised from the filtrate.



Properties of oxalic acid

When crystallised from water, colourless prismatic crystals of oxalic acid dihydrate, $(COOH)_2 . 2H_2O$, are obtained. The dihydrate melts at 101.5°C, while the anhydrous acid melts at 189.5°C. The hydrate acid becomes anhydrous when carefully heated to 150°C. Oxalic acid is an active poison, depressing the central nervous system and causing malfunction of kidneys.

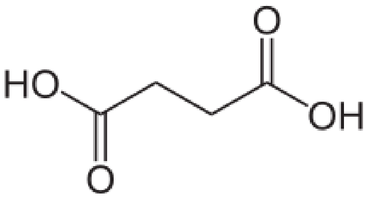
The oxalic acid molecule is made of two carboxyl groups in the direct union. It gives all the usual reactions of COOH group twice. Also, the acid gives some peculiar reactions which involve the cleavage of the weakened linkage between the two highly oxidised carbon atoms.

Uses of oxalic acid

1. For removing ink stains and for bleaching straw for hats, since it reduces brown ferric compounds to soluble and almost colourless ferrous salts.
2. As a mordant in dyeing and calico printing.
3. In the manufacture of inks and metal polishes.
4. For preparing allyl alcohol and formic acid in the laboratory.
5. In redox Titrations.

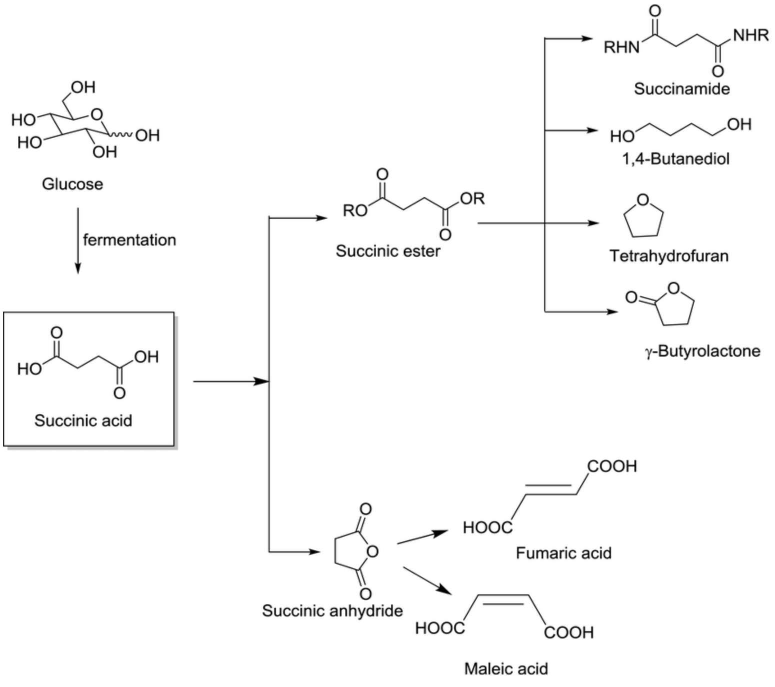
Preparation, proerties and uses of succinic acid

Succinic acid is a dicarboxylic acid with the chemical formula $(CH_2)_2(CO_2H)_2$. The name derives from Latin succinum, meaning amber. In living organisms, succinic acid takes the form of an anion, succinate, which has multiple biological roles as a metabolic intermediate being converted into fumarate by the enzyme succinate dehydrogenase in complex 2 of the electron transport chain which is involved in making ATP, and as a signaling molecule reflecting the cellular metabolic state.

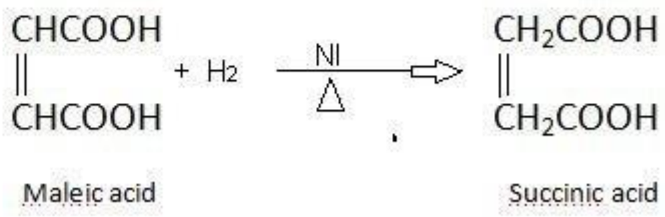


Preparation of succinic acid

Succinic acid was obtained from amber by distillation and known as spirit of amber. Common industrial routes include hydrogenation of maleic acid, oxidation of 1,4-butanediol, and carbonylation of ethylene glycol. Succinate is also produced from butane via maleic anhydride. Global production is estimated at 16,000 to 30,000 tons a year, with an annual growth rate of 10%. Genetically engineered Escherichia coli and Saccharomyces cerevisiae are proposed for the commercial production via fermentation of glucose.



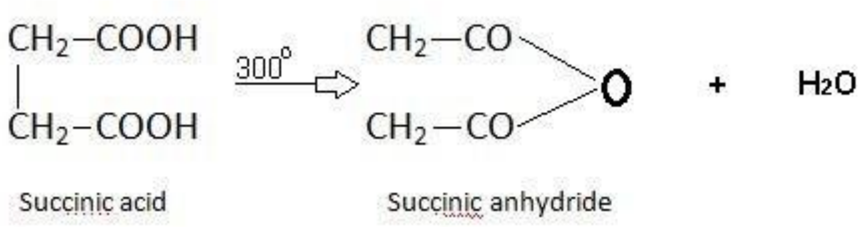
It is obtained industrially by catalytic reduction of maleic acid.



$$\begin{matrix} CHCOOH \\ \| \\ CHCOOH \end{matrix} + H_2 \xrightarrow[\Delta]{Ni} \begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix}$$

Properties of succinic acid

Succinic acid forms white monoclinic prisms, mp 188°C. It is soluble in ethyl alcohol and ether, but moderately soluble in water. Succinic acid gives all the normal reactions of a dicarboxylic acid.



Uses of succinic acid

It is a common organic acid, which can be used in many food, chemical, and pharmaceutical industries as a precursor to generate many chemicals such as solvents, perfumes, lacquers, plasticizer, dyes, and photographic chemicals. Succinic acid is also used as an antibiotic and curative agent.

UNIT-IV

ORGANOMETALLIC COMPOUNDS AND ORGANO SULPHUR COMPOUNDS

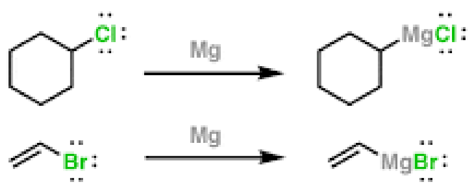
Grignard reagent

The discovery of the Grignard reaction in 1900 was awarded with the Nobel prize in 1912. For more details on the history see Victor Grignard. A Grignard reagent or Grignard compound is a chemical compound with the generic formula R−Mg−X, where X is a halogen and R is an organic group, normally an alkyl or aryl. Two typical examples are methylmagnesium chloride $Cl-Mg-CH_3$ and phenylmagnesium bromide $(C_6H_5)-Mg-Br$. They are a subclass of the organomagnesium compounds. Grignard compounds are popular reagents in organic synthesis for creating new carbon-carbon bonds. For example, when reacted with another halogenated compound R'−X' in the presence of a suitable catalyst, they typically yield R−R' and the magnesium halide MgXX' as a byproduct; and the latter is insoluble in the solvents normally used. In this aspect, they are similar to organolithium reagents. Pure Grignard reagents are extremely reactive solids. They are normally handled as solutions in solvents such as diethyl ether or tetrahydrofuran; which are relatively stable as long as water is excluded. In such a medium, a Grignard reagent is invariably present as a complex with the magnesium atom connected to the two ether oxygens by coordination bonds.

Synthesis of grignard reagent

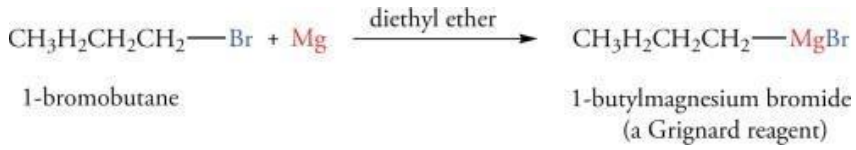
Traditionally Grignard reagents are prepared by treating an organic halide (normally organobromine) with magnesium metal. Ethers are required to stabilize the organomagnesium compound. Water and air, which rapidly destroy the reagent by protonolysis or oxidation, are excluded using air-free techniques. Although the reagents still need to be dry, ultrasound can allow Grignard reagents to form in wet solvents by activating the magnesium such that it consumes the water.

Example 1: Formation of Grignard reagents



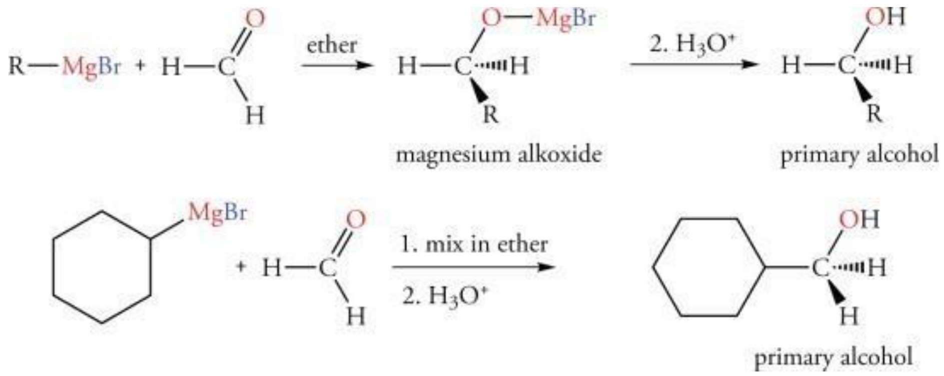
Grignards can be formed from alkyl or alkenyl chlorides, bromides or iodides (never fluorides)

Haloalkanes and aryl and vinyl halides react with magnesium metal to yield organomagnesium halides called Grignard reagents.

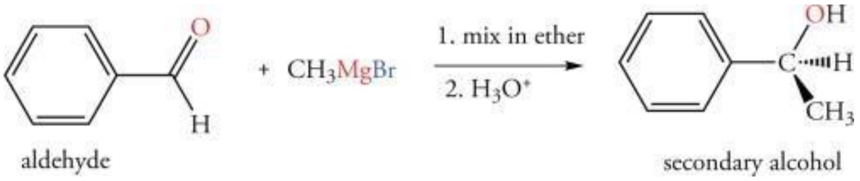


Properties of grignard reagent

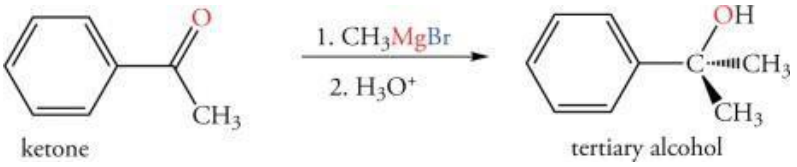
1. Grignard reagents add to carbonyl compounds to give primary, secondary, and tertiary alcohols. A primary alcohol is synthesized by reacting the Grignard reagent, R′─MgX, with formaldehyde.



2. Reacting a Grignard reagent with an aldehyde gives a secondary alcohol.



3. Reacting a Grignard reagent with a ketone gives a tertiary alcohol.



Uses of grignard reagent

1. Synthesis of hydrocarbons, acid, ketone and aldehydes.
2. Synthesis of ethers and esters
3. Preparation of organometalic compounds

4. Synthesis of primary, secondary and tertiary alcohols.

Preparation and properties of Methyllithium

Methyllithium is the simplest organolithium reagent with the empirical formula CH_3Li. This s-block organometallic compound adopts an oligomeric structure both in solution and in the solid state. This highly reactive compound, invariably used in solution with ether as the solvent, is a reagent in organic synthesis as well as organometallic chemistry. Operations involving methyllithium require anhydrous conditions, because the compound is highly reactive toward water. Oxygen and carbon dioxide are also incompatible with MeLi. Methyl lithium is usually not prepared, but purchased as a solution in various ethers.

1 Synthesis of Methyllithium

In the direct synthesis, methyl bromide is treated with a suspension of lithium in diethyl ether.

$$2\ Li + MeBr \rightarrow LiMe + LiBr$$

The lithium bromide forms a complex with the methyllithium. Most commercially available methyllithium consists of this complex. "Halide-free" methyllithium is prepared from methyl chloride. Lithium chloride precipitates from the diethyl ether since it does not form a strong complex with methyllithium. The filtrate consists of fairly pure methyllithium. Alternatively, commercial methyllithium can be treated with dioxane to precipitate LiBr, which can be removed by filtration.

Preparation and properties of thioalcohols

A thiol is any organosulfur compound of the form R−SH, where R represents an alkyl or other organic substituent. The –SH functional group itself is referred to as either a thiol group or a sulfhydryl group, or a sulfanyl group. Thiols are the sulfur analogue of alcohols. Many thiols have strong odors resembling that of garlic or rotten eggs. Thiols are used as odorants to assist in the detection of natural gas and the "smell of natural gas" is due to the smell of the thiol used as the odorant. Thiols show little association by hydrogen bonding, both with water molecules and among themselves. Hence, they have lower boiling points and are less soluble in water and other polar solvents than alcohols of similar molecular weight. For this reason also, thiols and their corresponding sulfide functional group isomers have similar solubility characteristics and boiling points, whereas the same is not true of alcohols and their corresponding isomeric ethers.

Preparation of thioalcohols

1. In industry, methanethiol is prepared by the reaction of hydrogen sulfide with methanol. This method is employed for the industrial synthesis of methanethiol.

$$CH_3OH + H_2S \rightarrow CH_3SH + H_2O$$

Such reactions are conducted in the presence of acidic catalysts. The other principal route to thiols involves the addition of hydrogen sulfide to alkenes. Such reactions are usually conducted in the presence of an acid catalyst or UV light. Halide displacement, using the suitable organic halide and sodium hydrogen sulfide has also been utilized.

2. Another method entails the alkylation of sodium hydrosulfide.

$$RX + NaSH \rightarrow RSH + NaX \ (X = Cl, Br, I)$$

This method is used for the production of thioglycolic acid from chloroacetic acid.

3. In general, on the typical laboratory scale, the direct reaction of a haloalkane with sodium hydrosulfide is inefficient owing to the competing formation of sulfides. Instead, alkyl halides are converted to thiols via an S-alkylation of thiourea. This multistep, one-pot process proceeds via the intermediacy of the isothiouronium salt, which is hydrolyzed in a separate step.

$$CH_3CH_2Br + SC(NH_2)_2 \rightarrow [CH_3CH_2SC(NH_2)_2]Br$$

$$[CH_3CH_2SC(NH_2)_2]Br + NaOH \rightarrow CH_3CH_2SH + OC(NH_2)_2 + NaBr$$

Properties of thioalcohols

Akin to the chemistry of alcohols, thiols form sulfides, thioacetals, and thioesters, which are analogous to ethers, acetals, and esters respectively. Thiols and alcohols are also very different in their reactivity, thiols being more easily oxidized than alcohols. Thiolates are more potent nucleophiles than the corresponding alkoxides.

1. S-Alkylation

Thiols, or more specific their conjugate bases, are readily alkylated to give sulfides:

$$RSH + R'Br + B \rightarrow RSR' + [HB]Br \ (B = base)$$

2. Acidity

Thiols are easily deprotonated. Relative to the alcohols, thiols are more acidic. The conjugate base of a thiol is called a thiolate. Butanethiol has a pK_a of 10.5 vs 15 for butanol. Thiophenol has a pK_a of 6, versus 10 for phenol. A highly acidic thiol is pentafluorothiophenol (C_6F_5SH) with a pK_a of 2.68. Thus, thiolates can be obtained from thiols by treatment with alkali metal hydroxides.

3. Redox

Thiols, especially in the presence of base, are readily oxidized by reagents such as bromine and iodine to give an organic disulfide (R−S−S−R).

$$2\ R{-}SH + Br_2 \rightarrow R{-}S{-}S{-}R + 2\ HBr$$

Uses of thioalcohols

1. Preparation of mercaptal
2. Synthesis of thioester

Preparation and properties of Thioether

A thioether is a functional group in organic chemistry that has the structure R1-S-R2 as shown on right. Like many other sulfur-containing compounds, volatile thioethers characteristically have foul odors. A thioether is similar to ether except that it contains a sulfur atom in place of the oxygen. Because oxygen and sulfur belong to the chalcogens group in the periodic table, the chemical properties of ethers and thioethers share some commonalities. This functional group is important in biology, most notably in the amino acid methionine and the cofactor biotin.

Preparation of Thioether

1. Thioethers are typically prepared by the alkylation of thiols:

$$R\text{-}Br + HS\text{-}R' \rightarrow R\text{-}S\text{-}R' + HBr$$

Such reactions are accelerated in the presence of base, which converts the thiol into the more nucleophilic thiolate.

2. An alternative method of synthesis includes the addition of a thiol to an alkene, typically catalysed by free radicals:

$$R\text{-}CH{=}CH_2 + HS\text{-}R' \rightarrow R\text{-}CH_2\text{-}CH_2\text{-}S\text{-}R'$$

Properties of Thioether

1. While ethers are generally stable, thioethers (R-S-R) are easily oxidized to the sulfoxides (R-S(=O)-R), which can themselves be further oxidized to sulfones (R-S(=O)$_2$-R). For example, dimethyl sulfide can be oxidized as follows:

$$S(CH_3)_2 + O \rightarrow OS(CH_3)_2$$
$$OS(CH_3)_2 + O \rightarrow O_2S(CH_3)_2$$

   Typical oxidants include peroxides.

2. The sulfur-sulfur bond in disulfides is susceptible to cleavage by nucleophiles, and reaction with a carbon nucleophile produces a thioether:

$$R_3C^- + R^1S\text{-}SR^2 \rightarrow R_3CSR^1 + R^2S^-$$

3. Trialkysulfonium salts react with nucleophiles with a dialkyl sulfide as a leaving group:

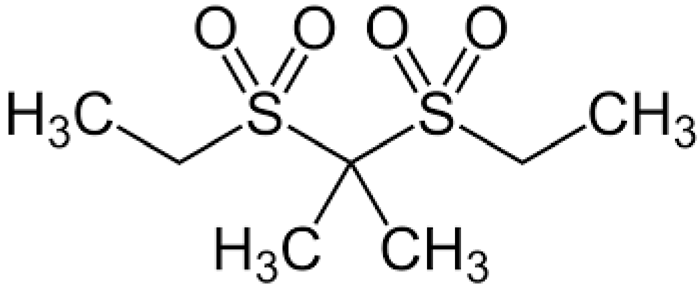
$$Nu^- + R_3S^+ \rightarrow Nu\text{-}R + R\text{-}S\text{-}R$$

Uses of Thioether

Dimethyl sulfide is the simplest thioether. It is used in important reactions like the Swern oxidation. This makes aldehydes starting from alcohols.

Sulphonal

Sulfonal is a chemical compound first synthesized by Eugen Baumann in 1888 and introduced as a hypnotic drug by Alfred Kast later on, but now superseded by newer and safer sedatives. Its appearance is either in colorless crystalline or powdered form.

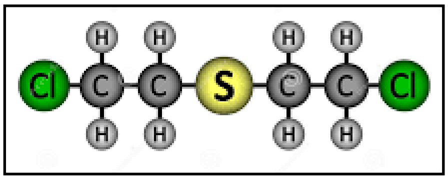


Preparation of Sulphonal

Sulfonal is prepared by condensing acetone with ethyl mercaptan in the presence of hydrochloric acid, the mercaptol $(CH_3)_2C(SC_2H_5)_2$ formed being subsequently oxidized by potassium permanganate. It is also formed by the action of alcoholic potash and methyl iodide on ethylidene diethyl sulfine, $CH_3CH(SO_2C_2H_5)_2$ (which is formed by the oxidation of dithioacetal with potassium permanganate). It crystallizes in prisms melting at 125 C, which are practically insoluble in cold water, but dissolve in 15 parts of hot and also in alcohol and ether.

Mustard Gas

Mustard gas or sulfur mustard is a chemical compound belonging to a family of cytotoxic and blister agents known as mustard agents. The name mustard gas is widely used, but it is technically incorrect: the substance, when dispersed, is often not actually in a vapor, but is instead in the form of a fine mist of liquid droplets. Sulfur mustards are viscous liquids at room temperature and have an odor resembling mustard plants, garlic, or horseradish, hence the name. When pure, they are colorless, but when used in impure forms, such as in warfare, they are usually yellow-brown.



1 Preparation of Mustard Gas

1. Mustard gas can be synthesized in a variety of different ways. In the Depretz method, sulfur dichloride is treated with ethylene:

$$SCl_2 + 2\ C_2H_4 \rightarrow (ClC_2H_4)_2S$$

2. Mustard gas can be readily decontaminated with strong bases, giving divinyl sulfide:

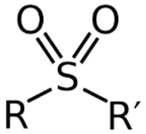
$$(ClC_2H_4)_2S + 2\ NaOH \rightarrow (CH_2{=}CH)_2S + 2\ H_2O + 2\ NaCl$$

Uses of Mustard Gas

1. Mustard gas was first used effectively in World War I by the German army against British and Canadian soldiers near Ypres, Belgium, in 1917 and later also against the French Second Army.

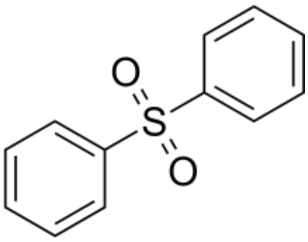
Sulphone

A sulfone is a chemical compound containing a sulfonyl functional group attached to two carbon atoms. The central hexavalent sulfur atom is double-bonded to each of two oxygen atoms and has a single bond to each of two carbon atoms, usually in two separate hydrocarbon substituents.



4,7,1 Diphenyl sulfone

Diphenyl sulfone is an organosulfur compound with the formula $(C_6H_5)_2SO_2$. It is a white solid that is soluble in organic solvents. It is used as a high temperature solvent. Such high temperature solvents are useful for processing highly rigid polymers, e.g., PEEK, which only dissolve in very hot solvents. It is produced by the sulfonation of benzene with sulfuric acid and oleum. For typical processes, benzenesulfonic acid is an intermediate. It is also produced from benzenesulfonyl chloride and benzene.

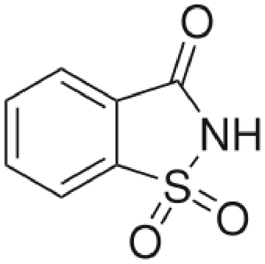


Application of Sulphone

1. Sulfolane is used to extract valuable aromatic compounds from petroleum
2. Some polymers containing sulfone groups are useful engineering plastics. They exhibit high strength and resistance to oxidation, corrosion, high temperatures, and creep under stress. For example, some are valuable as replacements for copper in domestic hot water plumbing. Precursors to such polymers are the sulfones bisphenol S and 4,4′-dichlorodiphenyl sulfone.
3. Examples of sulfones in pharmacology include dapsone, a drug formerly used as an antibiotic to treat leprosy, dermatitis herpetiformis, tuberculosis, or pneumocystis pneumonia (PCP). Several of its derivatives, such as promin, have similarly been studied or actually been applied in medicine, but in general sulfones are of far less prominence in pharmacology than for example the sulfonamides.

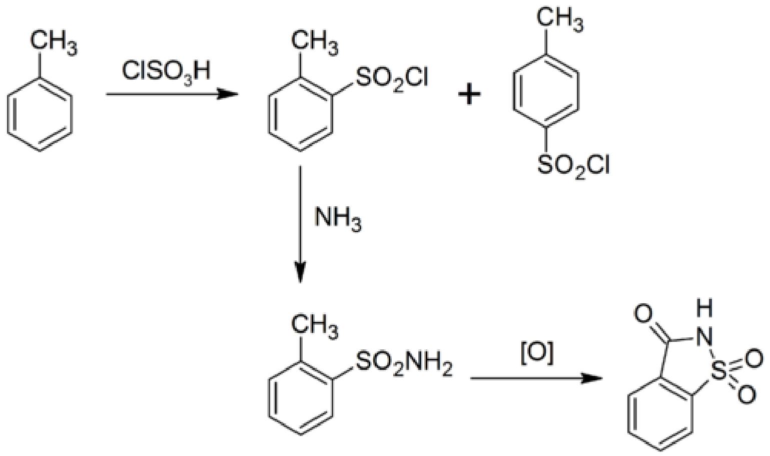
Synthesis and application of saccharin

Saccharin is an artificial sweetener with effectively no food energy. It is about 550 times as sweet as sucrose but has a bitter or metallic aftertaste, especially at high concentrations. Saccharin is used to sweeten products such as drinks, candies, cookies, and medicines.

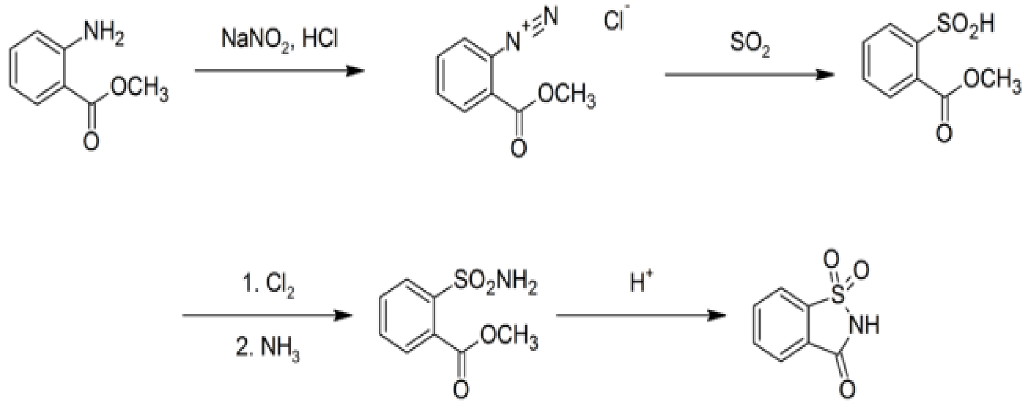


Preparation of saccharin

Saccharin can be produced in various ways. The original route by Remsen and Fahlberg starts with toluene; another route begins with o-chlorotoluene. Sulfonation of toluene by chlorosulfonic acid gives the ortho and para substituted sulfonyl chlorides. The ortho isomer is separated and converted to the sulfonamide with ammonia. Oxidation of the methyl substituent gives the carboxylic acid, which cyclicizes to give saccharin free acid.



In 1950, an improved synthesis was developed at the Maumee Chemical Company of Toledo, Ohio. In this synthesis, the methyl anthranilate successively reacts with nitrous acid, sulfur dioxide, chlorine, and then ammonia to yield saccharin.



Application of saccharin

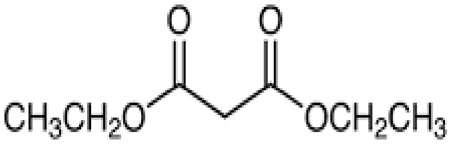
1. The substance is used as an artificial sweetening agent since its intensity of sweetness is much higher than that of sucrose but it isn´t metabolized and for that suitable for diabetics´ and dietary food.
2. Saccharin is one of the most affordable low-calorie sweeteners available. It's popular as a zero-calorie substitute for sugar in cooking. It's also used as a sweetener in low-calorie processed foods such as fruit juices, candies, jams, jellies, and cookies. Saccharin is sold in a variety of brand names.

UNIT-V

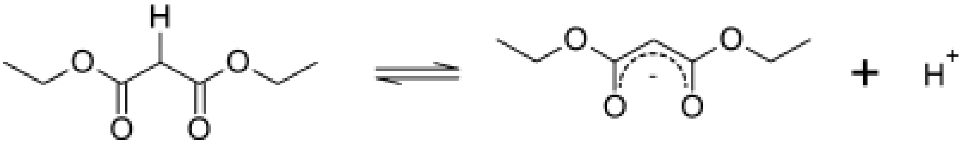
REACTIVE METHYLENE COMPOUNDS AND CONFORMATIONAL ISOMERS

Preparation and synthetic use of Diethyl malonate

Diethyl malonate, also known as DEM, is the diethyl ester of malonic acid. It occurs naturally in grapes and strawberries as a colourless liquid with an apple-like odour, and is used in perfumes. It is also used to synthesize other compounds such as barbiturates, artificial flavourings, vitamin B1, and vitamin B_6.

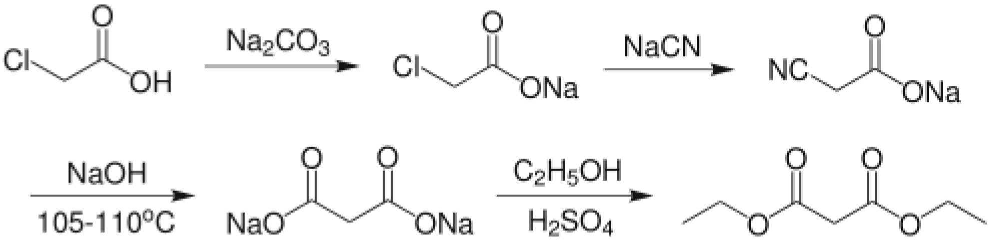


Malonic acid is a rather simple dicarboxylic acid, with two the carboxyl groups close together. In forming diethyl malonate from malonic acid, the hydroxyl group (−OH) on both of the carboxyl groups is replaced by an ethoxy group (−OEt; $-OCH_2CH_3$). The methylene group ($-CH_2-$) in the middle of the malonic part of the diethyl malonate molecule is neighboured by two carbonyl groups (−C(=O)−). The hydrogen atoms on the carbon adjacent to the carbonyl group in a molecule is significantly more acidic than hydrogen atoms on a carbon adjacent to alkyl groups The hydrogen atoms on a carbon adjacent to two carbonyl groups are even more acidic because the carbonyl groups help stabilize the carbanion resulting from the removal of a proton from the methylene group between them.



Preparation of Diethyl malonate

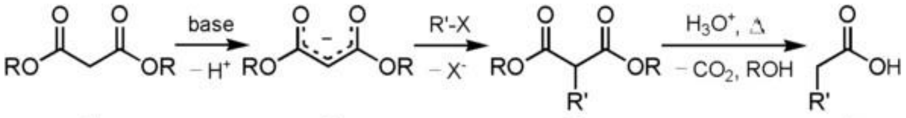
Diethyl malonate may be prepared by reacting the sodium salt of chloroacetic acid with sodium cyanide, followed by base hydrolysis of the resultant nitrile to give the sodium salt of the malonic acid. Fischer esterification gives diethyl malonate.



Properties of Diethyl malonate

❖ Malonic ester synthesis

One of the principal uses of this compound is in the malonic ester synthesis. The carbanion (2) formed by reacting diethyl malonate (1) with a suitable base can be alkylated with a suitable electrophile. This alkylated 1,3-dicarbonyl compound (3) readily undergoes decarboxylation with loss of carbon dioxide, to give a substituted acetic acid (4).



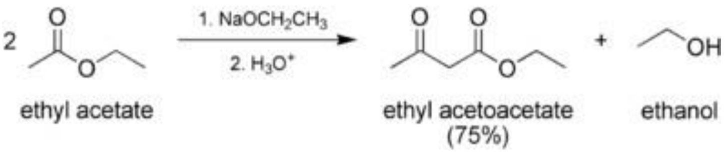
1 2 3 4

Preparation and synthetic use of ethyl acetoacetate

The organic compound ethyl acetoacetate (EAA) is the ethyl ester of acetoacetic acid. It is a colorless liquid. It is widely used as a chemical intermediate in the production of a wide variety of compounds. It is used as a flavoring for food.

Preparation of ethyl acetoacetate

Ethyl acetoacetate is produced industrially by treatment of diketene with ethanol. The preparation of ethyl acetoacetate is a classic laboratory procedure. It is prepared via the Claisen condensation of ethyl acetate. Two moles of ethyl acetate condense to form one mole each of ethyl acetoacetate and ethanol.



Properties of ethyl acetoacetate

1. Acidity

Ethyl acetoacetate is diprotic

$$CH_3C(O)CH_2CO_2Et + NaH \rightarrow CH_3C(O)CH(Na)CO_2Et + H_2$$

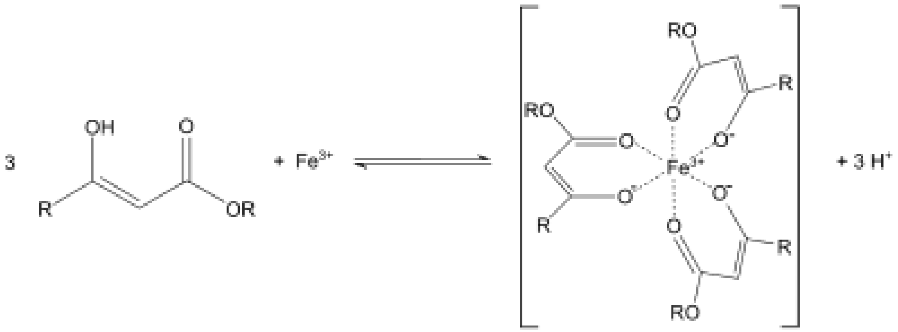
$$CH_3C(O)CH(Na)CO_2Et + BuLi \rightarrow LiCH_2C(O)CH(Na)CO_2Et + BuH$$

2. Keto-enol tautomerism

Ethyl acetoacetate is subject to keto-enol tautomerism. In the neat liquid at 33 °C, the enol consists of 15% of the total.

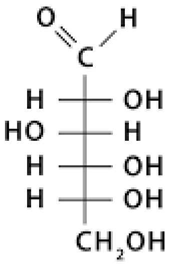
3. Ligand

Similar to the behavior of acetylacetone, the enolate of ethyl acetoacetate can also serve as a bidentate ligand. For example, it forms purple coordination complexes with iron(III) salts.

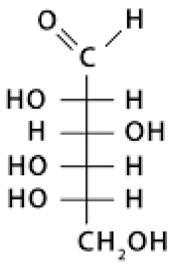


Fischer projection

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.



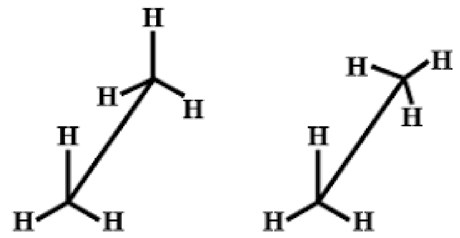
D- Glucose



L- Glucose

Sawhorse projections

A sawhorse projection is a view of a molecule down a particular carbon-carbon bond. Groups connected to both the front and back carbons are drawn using sticks at 120° angles. A saw-horse formula is a diagram used to depict a specific conformation of a molecule. Sawhorse projection, allows better visualization of the three-dimensional geometry between adjacent carbon atoms.

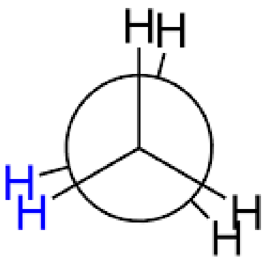


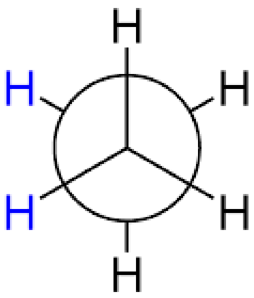
(i) Eclipsed (ii) Staggered

Sawhorse projections of ethane

Newman projections

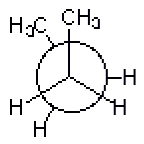
A Newman projection, useful in alkane stereochemistry, visualizes the conformation of a chemical bond from front to back, with the front atom represented by a dot and the back atom as a circle. The front atom is called proximal, while the back atom is called distal. This type of representation clearly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



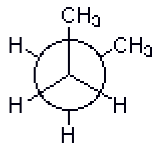


Dihedral angle

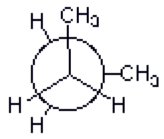
A dihedral angle is the angle between two intersecting planes or half-planes. In chemistry, it is the clockwise angle between half-planes through two sets of three atoms, having two atoms in common. In solid geometry, it is defined as the union of a line and two half-planes that have this line as a common edge. In higher dimensions, a dihedral angle represents the angle between two hyperplanes. The planes of a flying machine are said to be at positive dihedral angle when both starboard and port main planes are upwardly inclined to the lateral axis. When downwardly inclined they are said to be at a negative dihedral angle.



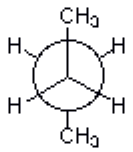
Dihedral angle = 0° or 360°



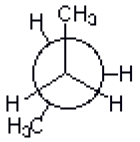
Dihedral angle = 60°



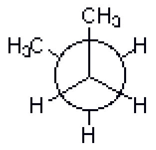
Dihedral angle = 120°



Dihedral angle = 180°



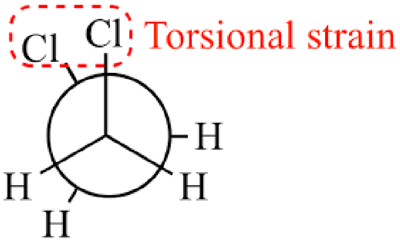
Dihedral angle = 240°



Dihedral angle = 300°

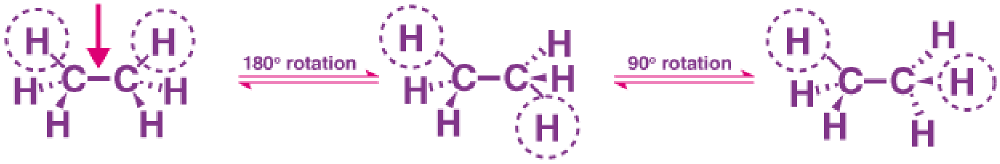
Torsional strain

Torsional strain is the resistance to bond twisting. In cyclic molecules, it is also called Pitzer strain. Torsional strain occurs when atoms separated by three bonds are placed in an eclipsed conformation instead of the more stable staggered conformation.



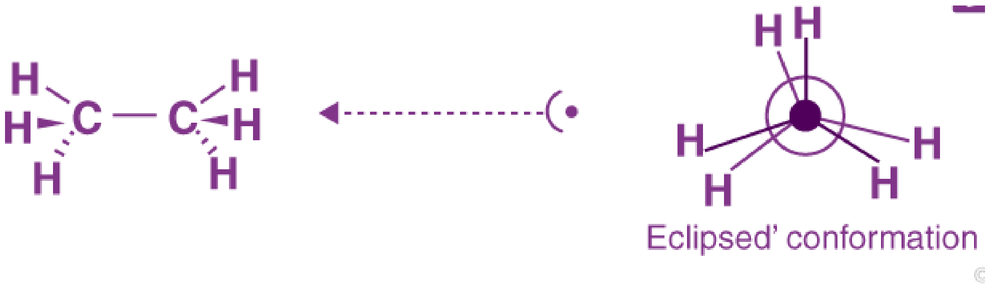
Conformations of Ethane

Ethane is an organic Chemical Compound. It is a colorless and odor gas at a standard temperature. Ethane molecule consists of seven sigma bonds. There will be a change in the shape of the molecule when there is a rotation of about six carbon-hydrogen bonds. But many possible differences occur when there is a rotation about the carbon-carbon bond.

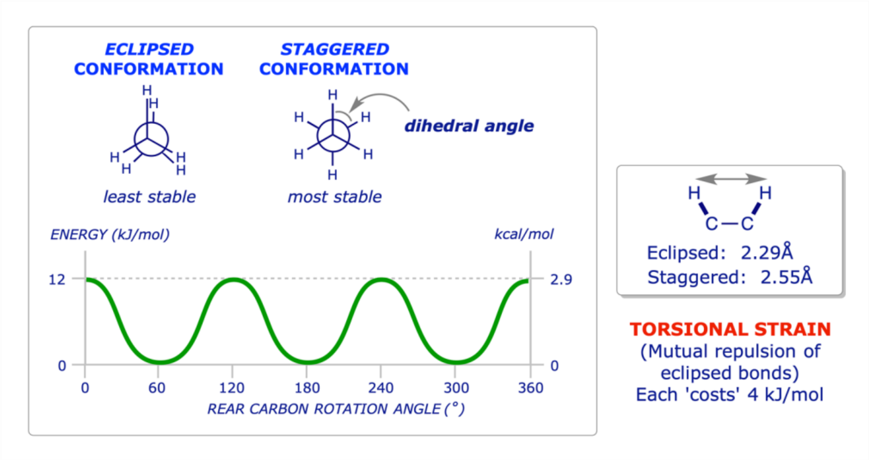


Now suppose we rotate [latex]CH{3}[/latex] group clockwise at an angle of 60 degrees, there would be a possible that hydrogen present at the front carbon is close to the hydrogen present at the back carbon. That is Eclipsed Conformation.

Eclipse Conformation is one of the highest Conformation. Another clockwise rotation at an angle of 60 degrees would lead to second eclipsed conformation. The solid line in the above figure represents the 6 carbon-hydrogen bond that is extended at an angle of 120 degrees from 2 carbons.

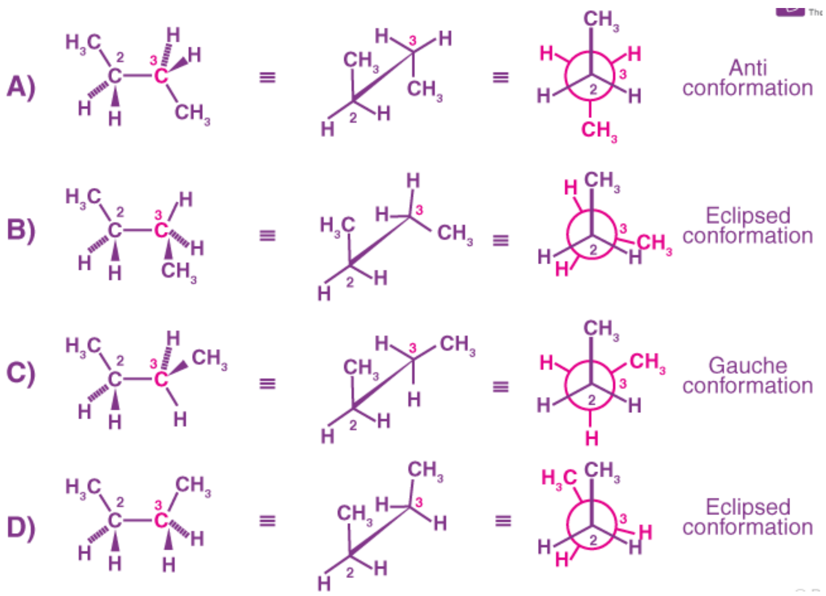


Uses of Ethane: it is widely used in the production of Ethane. It is mainly done through steam cracking. It acts as a ripening agent for food. It is a primary ingredient in mustard gas.

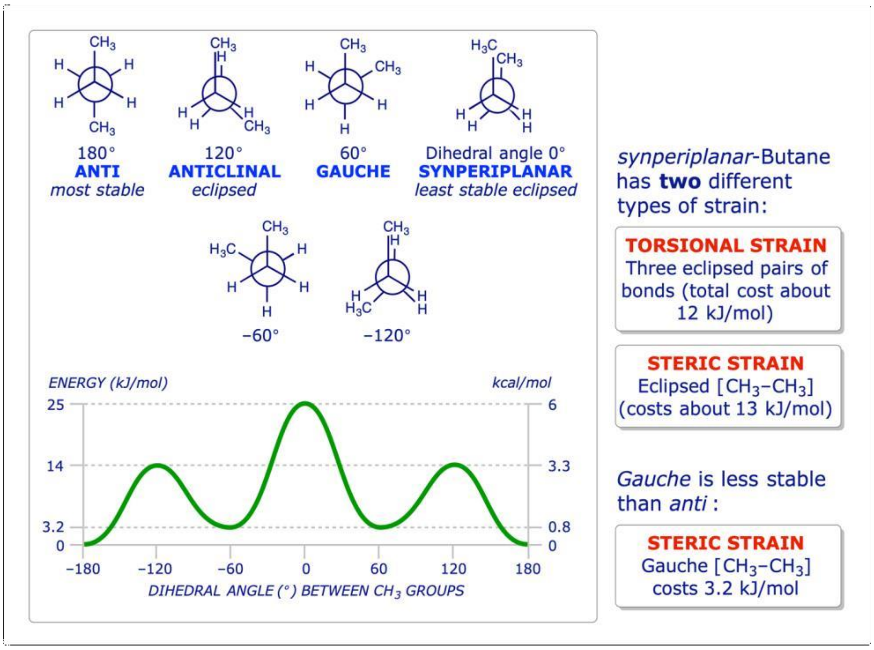


Conformations of Butane

Butane is an organic compound which consists of an alkane with 4 carbon atoms. It may refer to a mixture of 3 isomers. At atmospheric pressure, Butane is a gas. They are liquefied gas that is highly flammable. Compared to ethane, hydrogen butane consists of the complex set of conformations that is related to the constitution.



The below figure represents the 4 conformations of butane. The above diagram explains the rotation about C2-C3 bond due to the change in potential energy.



synperiplanar-Butane has **two** different types of strain:

TORSIONAL STRAIN
Three eclipsed pairs of bonds (total cost about 12 kJ/mol)

STERIC STRAIN
Eclipsed [CH_3–CH_3] (costs about 13 kJ/mol)

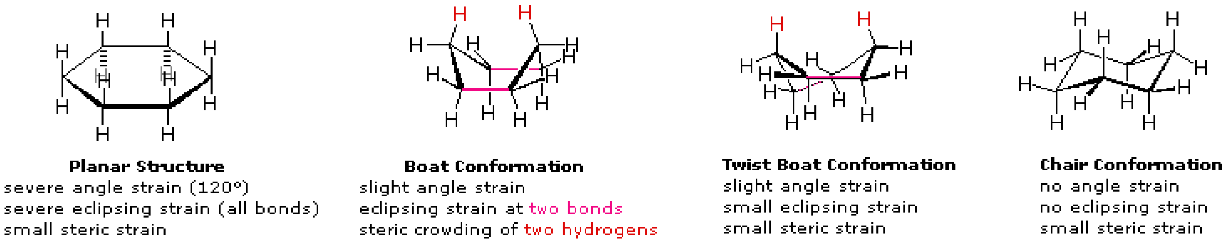
Gauche is less stable than *anti* :

STERIC STRAIN
Gauche [CH_3–CH_3] costs 3.2 kJ/mol

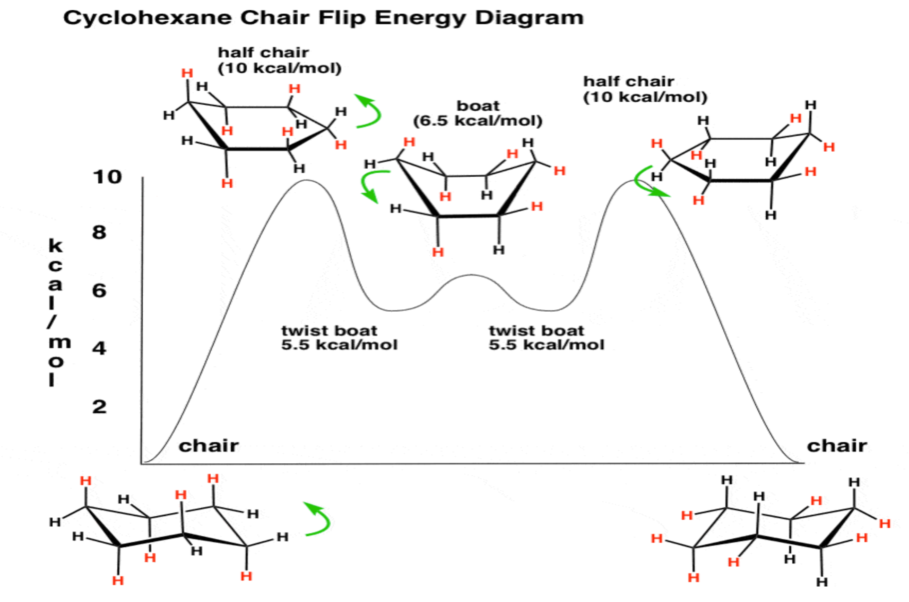
Uses of Butane: Pure of butane can be used as a refrigerant. It is used in Butane Torch. It is widely used in gasoline blending. Butane Cartridges are used to powered cordless hair irons.

Conformations of Cyclohexane

Cyclohexane has a non-polar structure that makes it almost free from ring strain. The most important conformations that it can have included chain conformation and boat conformation. The chair conformation is more stable than the boat conformation. The boat conformation can sometimes be more stable than it is usually, by a slight rotation in the C-C bonds and is called the skew boat conformation.



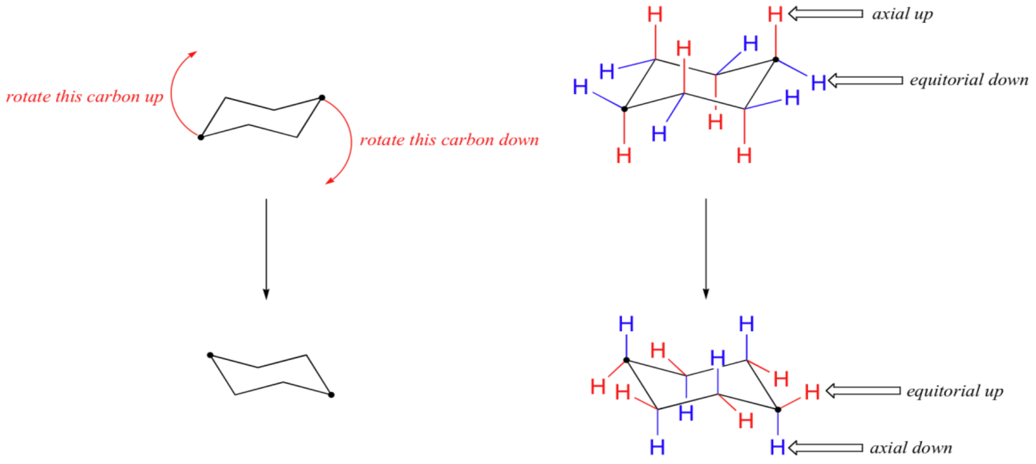
Nevertheless, the chair conformation is the most stable cyclohexane form. A regular hexagon shape contains internal angles of 120o. However, the carbon-carbon bonds belonging to the cyclohexane ring have a tetrahedral symmetry, with the bond angles corresponding to 109.5o. This is the reason why the cyclohexane ring has a tendency to take up several warped conformations (so that the bond angles are brought closer to the tetrahedral angle (109.5o) and there is reduced overall strain energy).



Examples of common conformations of cyclohexane include the boat, the twist-boat, the chair, and the half-chair conformations, which are named based on the shape that the cyclohexane molecule assumes in them. These four cyclohexane conformations have been illustrated below along with some insight on their stability. A Conformation of cyclohexane can refer to many 3-Dimensional shapes assumed by a cyclohexane molecule without disturbing the integrity of the chemical bonds in it.

Axial and Equatorial bonds

The chair conformation of cyclohexane, shows that the twelve hydrogens are not structurally equivalent. Six of them are located about the periphery of the carbon ring, and are termed equatorial. The other six are oriented above and below the approximate plane of the ring (three in each location), and are termed axial because they are aligned parallel to the symmetry axis of the ring.



Ring flipping

in organic chemistry, a ring flip (also known as a ring inversion or ring reversal) is the interconversion of cyclic conformers that have equivalent ring shapes (e.g., from a chair conformer to another chair conformer) that results in the exchange of nonequivalent substituent positions.[1] The overall process generally takes place over several steps, involving coupled rotations about several of the molecule's single bonds, in conjunction with minor deformations of bond angles. Most commonly, the term is used to refer to the interconversion of the two chair conformers of cyclohexane derivatives, which is specifically referred to as a chair flip, although other cycloalkanes and inorganic rings undergo similar processes.