D.N.R.COLLEGE (AUTONOMOUS): BHIMAVARM

DEPARTMENT OF PG CHEMISTRY

ORGANIC REACTION MECHANISM-II&ORGANIC PHOTO CHEMISTRY

IV SEMESTER

Presented By

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DNR COLLEGE BHIMAVARAM

SEMESTER-IV

ORGANIC REACTION MECHANISM-II &

ORGANIC PHOTOCHEMISTRY

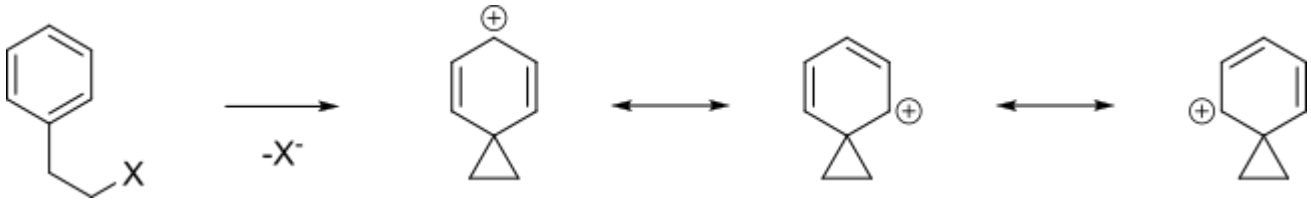
Neighbouring group assistance (NGA) in free radical reactions is a phenomenon observed in organic chemistry where a neighbouring functional group facilitates or accelerates a radical reaction. This assistance can significantly alter the reaction pathway and is crucial in various synthetic and biological processes. Here's a detailed overview:

Understanding Neighbouring Group Assistance (NGA):

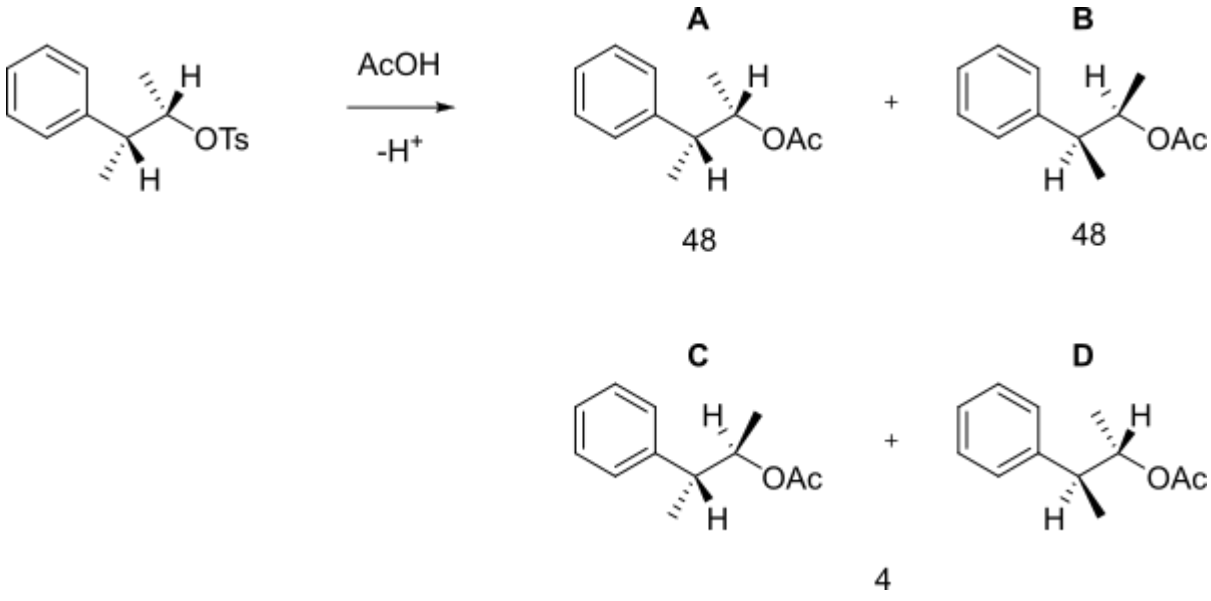
1. **Conceptual Basis**:
    - Neighbouring group assistance occurs when a nearby functional group stabilizes or reacts with a radical intermediate, thereby lowering the activation energy of the reaction.
    - It can lead to selective reaction pathways and enhanced reaction rates.
2. **Types of Neighbouring Group Assistance**:
    - **Electron Donating Groups**: Functional groups that donate electrons to stabilize radicals, such as alkyl groups (-CH3, -C2H5).
    - **Electron Withdrawing Groups**: Functional groups that stabilize radicals through resonance or inductive effects, like carbonyl groups (-C=O), nitro groups (-NO2), etc.
    - **Cyclization and Ring Formation**: Where the proximity of the neighbouring group allows for intramolecular reactions, leading to ring closure (cyclization reactions).
3. **Mechanistic Insights**:
    - **Radical Stabilization**: The neighbouring group can stabilize the developing radical through resonance, inductive effects, or hyperconjugation.
    - **Transition State Stabilization**: By interacting with the transition state of the reaction, the neighbouring group can lower the activation energy.
    - **Steric Effects**: Sometimes, the neighbouring group might also impose steric constraints that affect the reaction pathway.

NGP By an aromatic ring:

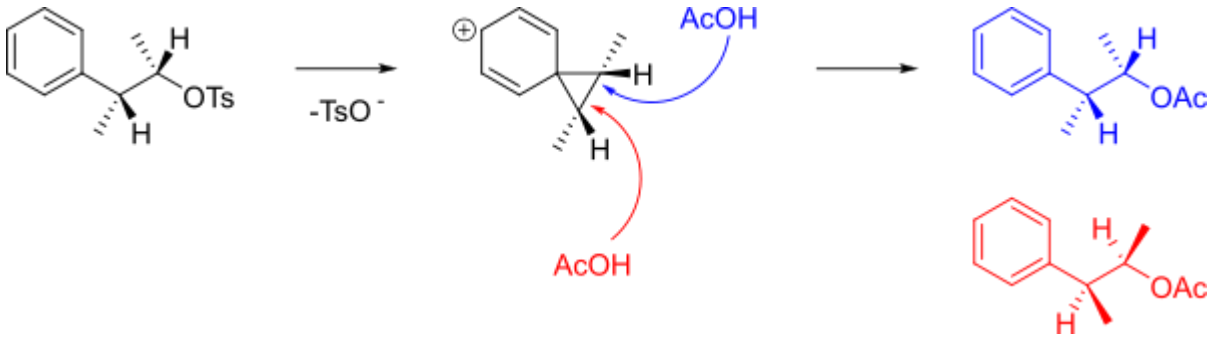
An aromatic ring can assist in the formation of a carbocationic intermediate called a **phenonium ion** by delocalising the positive charge.



When the following tosylate reacts with acetic acid in solvolysis then rather than a simple S_N2 reaction forming B, a 48:48:4 mixture of A, B (which are enantiomers) and C+D was obtained [2] [3].



The mechanism which forms A and B is shown below.



SANDMEYER REACTION:

The Sandmeyer reaction is a fundamental organic reaction used to convert aromatic diazonium salts into various functional groups, such as halides, cyanides, and hydroxylamines. Here are detailed notes on the Sandmeyer reaction:

Overview of the Sandmeyer Reaction:

1. **Reaction Type**:
    - The Sandmeyer reaction is a substitution reaction that transforms an aromatic diazonium salt (ArN_2^+) into a new functional group by substituting the diazonium group.
2. **Key Steps**:
    - **Diazotization**: The aromatic amine ($ArNH_2$) is treated with nitrous acid (HNO_2) and a source of nitrite ions (usually sodium nitrite, $NaNO_2$) under acidic conditions to form the diazonium salt (ArN_2^+).
    - **Substitution**: The resulting diazonium salt can then undergo substitution with various nucleophiles, leading to the formation of different functional groups.
3. **Mechanism**:

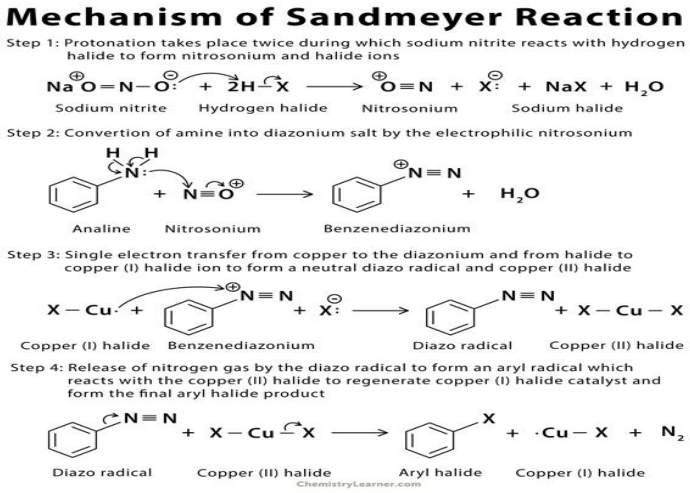
Diazotization: In acidic conditions, nitrous acid (HNO_2) converts the primary aromatic amine ($ArNH_2$) into the diazonium ion (ArN_2^+) by reacting with $NaNO_2$.

Substitution Reactions: The diazonium salt can undergo several types of substitution reactions:

Replacement with Halides: Treatment with copper salts (CuX) replaces the diazonium group with halides (X = Cl, Br, I).

Replacement with Cyanide: Using potassium cyanide (KCN) or copper cyanide (CuCN) replaces the diazonium group with a cyanide group (-CN).

Replacement with Hydroxylamine: Treatment with hydroxylamine (NH_2OH) replaces the diazonium group with a hydroxylamine group (-NHOH).



Safety Considerations:

Nitrous acid (HNO2) and its derivatives are toxic and can decompose explosively under certain conditions. Proper safety measures, including appropriate ventilation and protective equipment, should be observed when handling these reagents.

Example:

- **Formation of Chlorobenzene from Benzenediazonium Chloride**:
    1. Benzenediazonium chloride is prepared by diazotization of aniline with HNO2 and NaNO2 in HCl.
    2. Treatment with CuCl or CuBr replaces the diazonium group with a chlorine atom, yielding chlorobenzene.

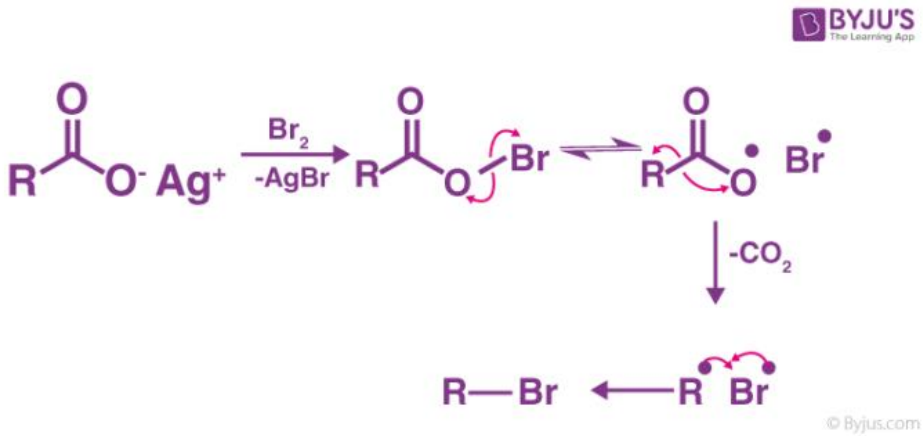
HUNSDIECKER REACTION:

The Hunsdiecker reaction is a transformation where a silver salt of a carboxylic acid reacts with a halogen (typically bromine or chlorine) to produce an alkyl halide one carbon shorter than the original carboxylic acid. Here are detailed notes on the Hunsdiecker reaction, including equations:

Overview of the Hunsdiecker Reaction:

1. **Reaction Type**:
    - The Hunsdiecker reaction is a decarboxylation reaction combined with a halogenation reaction. It converts a silver salt of a carboxylic acid into an alkyl halide.
2. **Key Steps**:
    - **Formation of Silver Carboxylate**: The carboxylic acid (RCO2H) is treated with silver oxide (Ag2O) to form a silver carboxylate (R-CO2Ag).

- **Reaction with Halogen**: The silver carboxylate is then treated with a halogen (commonly Br2 or Cl2), leading to the decarboxylation o



of the carboxylate group and the halogenation of the adjacent carbon.

3. **Mechanism**:
   - **Formation of Silver Carboxylate**:
   - RCOOH+Ag2O→RCOOAg+H2O
   - RCOOAg+Br2→RBr+CO2+AgBr
   - Here, RBr is the alkyl bromide product, CO2 is carbon dioxide, and AgBr is silver bromide, which precipitates out.
4. **Stereochemistry**:
   - The reaction typically proceeds with retention of stereochemistry at the alpha carbon (the carbon adjacent to the carboxylate group).
5. **Scope and Limitations**:
   - The Hunsdiecker reaction is effective for primary and secondary carboxylic acids, where the resulting alkyl halides are useful intermediates in organic synthesis.
   - Tertiary carboxylic acids do not generally undergo this reaction due to stability issues with the tertiary carbocations formed during the process.

Example:

- **Hunsdiecker Reaction with Silver Acetate (CH3COOAg) and Bromine (Br2)**:
  1. Silver acetate (CH3COOAg) is prepared from acetic acid (CH3COOH) and silver oxide (Ag2O).
  2. Treatment of silver acetate with bromine (Br2) results in the formation of methyl bromide (CH3Br), carbon dioxide (CO2), and silver bromide (AgBr):

$$CH3COOAg+Br2 \rightarrow CH3Br+CO2+AgBr$$

GOMBERG-BACHMANN REACTION

The Gomberg-Bachmann reaction, also known as aryl diazonium salt coupling or aryl diazonium coupling, is a method to introduce aryl groups onto aromatic rings through the reaction of aryl diazonium salts with aromatic compounds. Here are detailed notes on the Gomberg-Bachmann reaction:

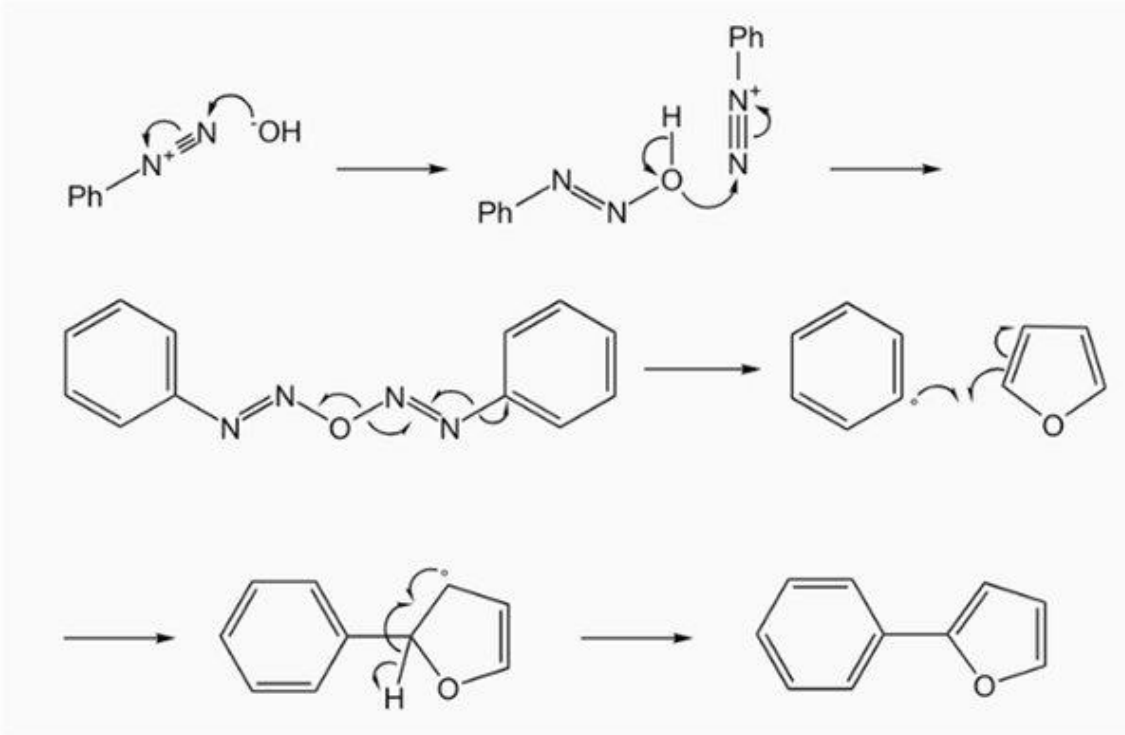
Overview of the Gomberg-Bachmann Reaction:

1. **Reaction Type**:
   - The Gomberg-Bachmann reaction is a coupling reaction where an aryl diazonium salt reacts with an aromatic compound to form a biaryl product.
2. **Key Steps**:
   - **Formation of Aryl Diazonium Salt**: An aromatic amine is diazotized using nitrous acid (HNO2) and a nitrite salt (NaNO2) under acidic conditions to form the aryl diazonium salt (ArN2+).
   - **Coupling Reaction**: The aryl diazonium salt then undergoes a nucleophilic aromatic substitution (SNAr) reaction with another aromatic compound (Ar') to form a new carbon-carbon bond between the two aromatic rings.
3. **Mechanism**:
   - **Diazotization**:

     $$ArNH2+HNO2+NaNO2 \rightarrow ArN_2^+ +NaOH+N2+H2O$$

   - Here, ArNH2 is the aromatic amine, ArN_2^+ is the aryl diazonium salt, and NaOH is sodium hydroxide formed as a byproduct.
   - **Coupling Reaction**:
   - $ArN_2^+ + Ar' \rightarrow Ar-Ar' + N_2$

     This reaction forms a biaryl compound (Ar-Ar') with the elimination of nitrogen gas.



4. **Scope and Limitations**:
    - The Gomberg-Bachmann reaction is particularly useful for forming symmetrical biaryl compounds where both aromatic rings are identical.
    - It is effective for a wide range of aromatic compounds, provided they are sufficiently nucleophilic to undergo the coupling reaction with the aryl diazonium salt.

Example:

- **Formation of Biphenyl from Aryl Diazonium Salt and Benzene**:
    1. Aniline ($C_6H_5NH_2$) is diazotized to form the diazonium salt ($C_6H_5N_2^+$).
    2. The diazonium salt reacts with benzene (C_6H_6) via electrophilic aromatic substitution to form biphenyl (C_6H_5-C_6H_5) and nitrogen gas (N_2):

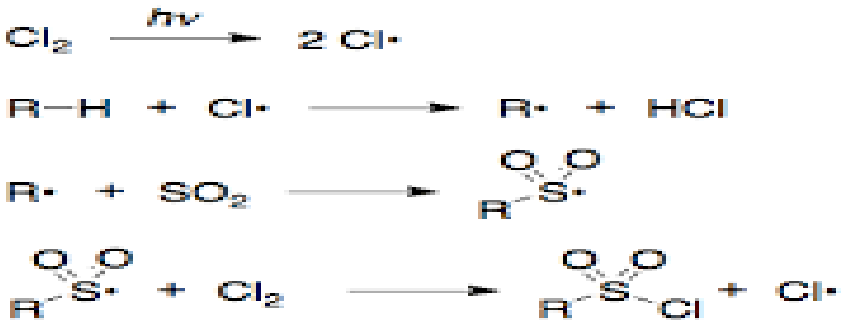
$$C_6H_5N_2^+ + C_6H_6 \rightarrow C_6H_5 - C_6H_5 + N_2$$

REED REACTION:

The chloro sulphonation of organic moilecules with chlorine and sulphurdioxide is called the Reed reaction.

$$RH+SO2+Cl2 \rightarrow RSO2Cl+HCl$$

Mechanism:



UNIT-II METHODOlOGIES IN ASYMMETRIC SYNTHESIS

Asymmetric synthesis: The direct synthesis of an optically active substance from optically inactive compound with (or) without the use of optically active agents is called asymmetric synthesis.

CLASSIFICATION OF ASYMMETRIC SYNTHESIS:

The basic principle of asymmetric synthesis is by using chiral substrates,chiral auxillary,chiral reagent,chiral catalyst we can produce unequal ratio of stereo isomers.

Asymmetric synthesis can create a new chiral centre,based on the nature of the compounds,the asymmetric synthesis is divided into 4 types.

1. chiral substrates controlled asymmetric synthesis.
2. chiral auxillary controlled asymmetric synthesis.
3. chiral reagent controlled asymmetric synthesis.
4. chiral catalyst controlled asymmetric synthesis.

Chiral substrates controlled asymmetric synthesis:

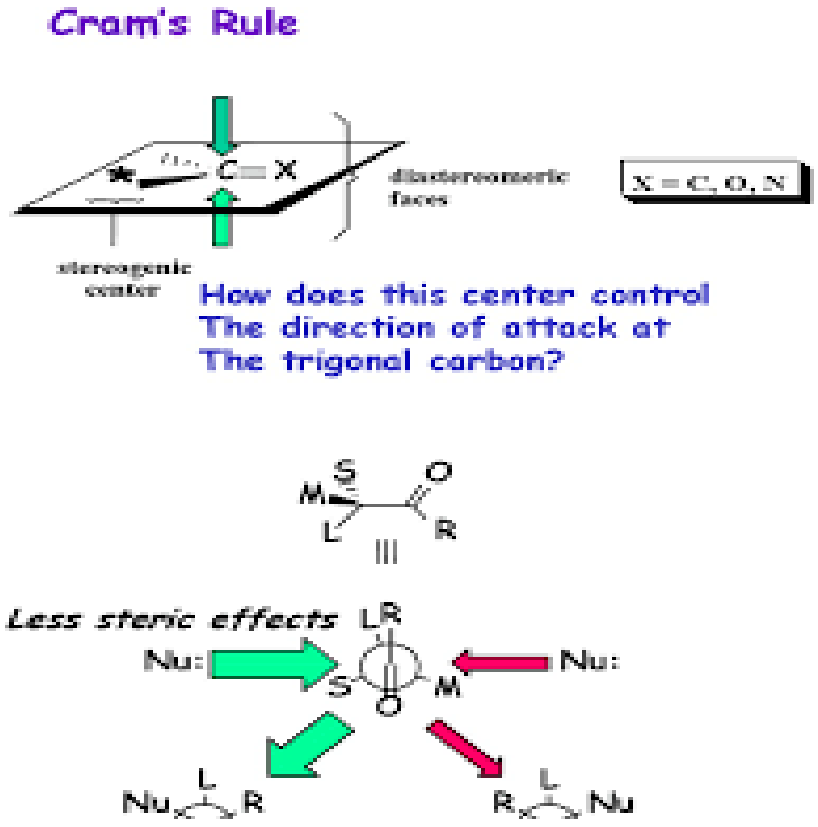
Chiral substrate controlled asymmetric synthesis, also known as substrate-controlled stereoselective synthesis, is a method in organic chemistry used to preferentially form one enantiomer or diastereomer over another in a chemical reaction. This is achieved by utilizing the intrinsic chirality of the substrate itself to direct the stereochemical outcome of the reaction.

Applications

- **Pharmaceuticals**: The synthesis of chiral drugs often relies on substrate-controlled methods to ensure the correct stereochemistry, which is crucial for the drug's efficacy and safety.
- **Natural Product Synthesis**: Many natural products are chiral and require precise stereochemical control in their synthesis, which can be achieved through substrate-controlled methods.
- **Agricultural Chemicals**: Chiral pesticides and herbicides often require enantiomerically pure compounds for selective activity and reduced environmental impact.

Cram's Rule

Cram's rule states that the nucleophile will preferentially attack the carbonyl group from the less hindered side, leading to the formation of the major diastereomer. The rule can be explained using the concept of steric hindrance and the preferred orientation of substituents around the chiral center.



Mechanism

1. **Chiral Center and Carbonyl Group**: Consider a molecule with a chiral center adjacent to a carbonyl group. The substituents on the chiral center are usually labeled as the largest group (L), the medium group (M), and the smallest group (S).
2. **Preferred Orientation**: In the transition state of the nucleophilic addition, the molecule adopts a conformation where the largest group (L) is positioned anti to the carbonyl group to minimize steric hindrance.
3. **Attack of the Nucleophile**: The nucleophile attacks the carbonyl carbon from the side opposite to the largest group (L), typically leading to the formation of the less sterically hindered product.

Example:Reduction of a Chiral Ketones:

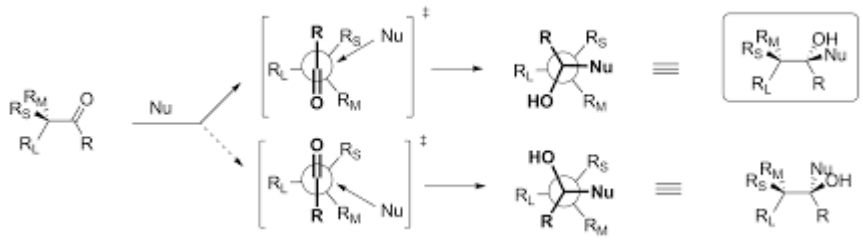
Let's consider the reduction of 2-phenylpropanal (PhCH(CH3)CHO) using a hydride donor like LiAlH4.

1. **Structure**: The molecule has a phenyl group (Ph), a methyl group (CH3), and a hydrogen atom (H) attached to the chiral center.
2. **Preferred Conformation**: The phenyl group (Ph) is the largest group, so it adopts an anti position relative to the carbonyl (C=O).
3. **Hydride Attack**: The hydride attacks from the side opposite to the phenyl group, leading to the major diastereomer where the hydride adds to the less hindered side.

Key Concepts and Mechanisms

1. **Intrinsic Chirality of the Substrate**: The starting material (substrate) possesses one or more chiral centers that influence the formation of new chiral centers in the product. The spatial arrangement of the substituents around the existing chiral center(s) controls the approach and reactivity of reagents.
2. **Steric and Electronic Effects**: The chiral centers in the substrate create a unique steric and electronic environment that can favor the formation of one stereoisomer over others. Steric hindrance can block certain pathways, while electronic factors can stabilize transition states leading to selective product formation.
3. **Diastereoselectivity and Enantioselectivity**:
    - **Diastereoselectivity**: When the reaction creates new chiral centers and the product has multiple chiral centers, the reaction is diastereoselective if it prefers the formation of one diastereomer over others.
    - **Enantioselectivity**: When the reaction preferentially produces one enantiomer over the other, it is enantioselective.

Felkin Anh model: The Felkin-Ahn model expands on the Felkin model by better explaining how aldehydes will react. First, the Felkin-Ahn model points out that the nucleophile will attack at a bond angle of 107 degrees, not 90 degrees. So, it needs to be 107 degrees away from the carbon-oxygen bond.



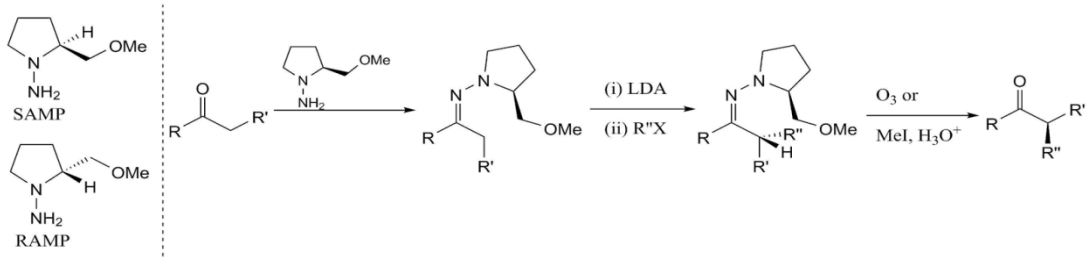
BY RAJAT CHALTA

Felkin Anh	Cram
No elapsing strain is present between □ carbonyl substituent and other substituent	Elapsing strain is present between □ carbonyl substituent and other substituent
Oxygen atom goes perpendicular to large group.	Oxygen remain as far as pssible from large group.
Diastereoselectivity depend on size □ carbonyl substituent .	Diastereoselectivity independent of size of □ carbonyl substituent .
Nucleophile attack from side between small and medium group .	Nucleophile attack from side between small and large group .

Chiral auxiliary controlled asymmetric synthesis:

Chiral auxiliary is an external optically pure chemical substance.It temporarily develops a complex with substrate and directs asymmetric synthesis.

And it is again regenerated after completion of the reaction.Generally it is denoted as "L*".Chiral auxiliary is responsible for formation of unequal ratio of products formation in the reaction.



Chiral reagent controlled asymmetric synthesis:

Chiral reagents can form energetically different TS's when approaching prochiral faces or groups on a molecule,and thus perform enantioselective reqctions directly on an achiral starting material.

Example:

Asymmetric reductions using BINAL-H (Alpine Borane) are a powerful method for achieving high enantioselectivity in the reduction of prochiral ketones and other carbonyl compounds. BINAL-H stands for B-isopinocampheyl-9-borabicyclo[3.3.1]nonane, and it exists in two enantiomeric forms, (R)- and (S)-BINAL-H, which can be used to induce chirality in the product.

Mechanism of Asymmetric Reduction with BINAL-H

1. **Formation of the BINAL-H Complex**: BINAL-H, a chiral borane reagent, forms a complex with the carbonyl compound. This complexation is crucial for the transfer of chirality.
2. **Stereoselective Hydride Transfer**: The hydride transfer occurs from the boron-hydrogen bond to the carbonyl carbon. The chirality of the boron complex dictates the approach of the hydride, leading to a preferential formation of one enantiomer over the other.
3. **Release of the Alcohol Product**: The product, a secondary alcohol, is released from the borane complex, and the borane is typically recycled or used in subsequent reactions.

Key Features

- **High Enantioselectivity**: The reduction often proceeds with high enantioselectivity due to the chiral environment provided by the BINAL-H reagent.
- **Mild Reaction Conditions**: The reductions typically occur under mild conditions, which helps preserve the integrity of sensitive functional groups.
- **Wide Applicability**: BINAL-H can be used for a variety of carbonyl compounds, including ketones and aldehydes.

Example: Reduction of Acetophenone

Let's consider the asymmetric reduction of acetophenone using (R)-BINAL-H

1. **Initial Complex Formation**: Acetophenone forms a complex with (R)-BINAL-H.
2. **Hydride Transfer**: The hydride is transferred from the borane to the carbonyl carbon. The (R)-BINAL-H directs the hydride to one face of the planar carbonyl group, preferentially forming one enantiomer over the other.
3. **Product Release**: The product, (R)-1-phenylethanol, is released with high enantioselectivity.

Mechanism

To visualize the mechanism, consider the following simplified steps:

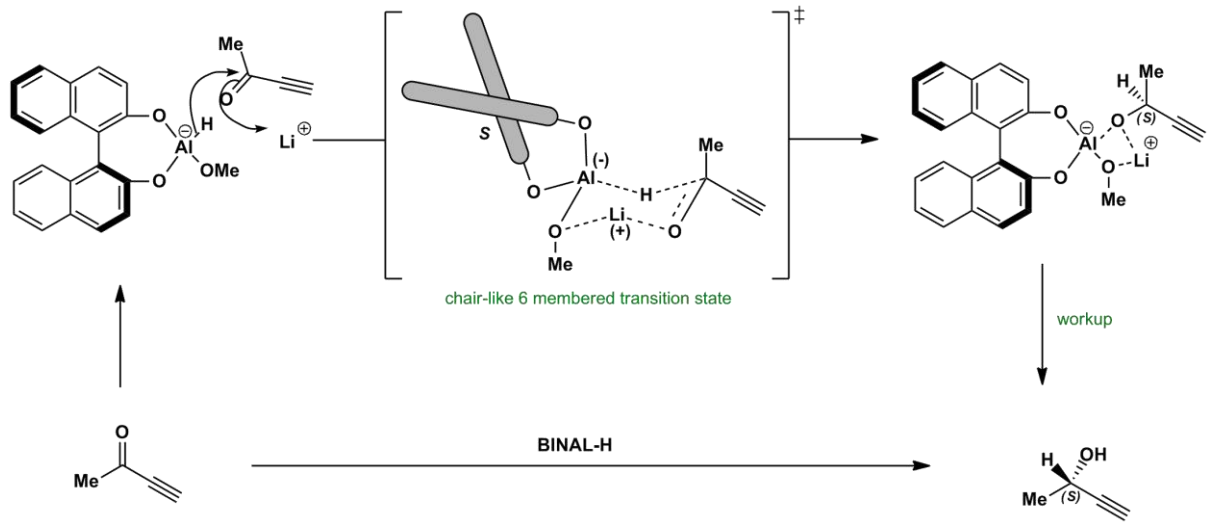
1. **Complex Formation**:

   PhCOCH3+(R)-BINAL-H→[PhCOCH3·(R)-BINAL-H]

2. **Hydride Transfer**:

   [PhCOCH3·(R)-BINAL-H]→PhCH(OH)CH3+BINAL-H

The hydride transfer is stereoselective due to the chiral environment provided by BINAL-H, leading to the preferential formation of one enantiomer.



2.Asymmetric hydroboration using diisopinocampheylborane (Ipc_2BH) is a method for converting alkenes into chiral alcohols with high enantioselectivity. Ipc_2BH is a chiral borane reagent derived from the naturally occurring compound pinene, and it is available in both (R)- and (S)-enantiomeric forms.

Mechanism of Asymmetric Hydroboration with Ipc_2BH

1. **Formation of the Borane-Alkene Complex**: The alkene coordinates to the chiral borane reagent, forming a transient complex. The steric and electronic properties of the chiral borane dictate the orientation of the alkene in this complex.
2. **Syn Addition**: The boron atom and a hydrogen atom add to the same face of the alkene in a concerted syn addition. This step is stereospecific and highly influenced by the chiral environment of the borane reagent.
3. **Oxidative Workup**: The resulting organoborane intermediate is typically oxidized using hydrogen peroxide (H_2O_2) in an alkaline medium

(NaOH), converting the boron moiety to a hydroxyl group and yielding the chiral alcohol.

Key Features

- **High Enantioselectivity**: The chiral environment provided by Ipc_2BH ensures that the addition of boron and hydrogen to the alkene occurs with high enantioselectivity.
- **Mild Reaction Conditions**: The hydroboration-oxidation sequence generally proceeds under mild conditions, preserving sensitive functional groups.
- **Wide Substrate Scope**: Ipc_2BH can be used with various alkenes, including terminal and internal alkenes, to produce a wide range of chiral alcohols.

Example: Hydroboration of Styrene

Let's consider the asymmetric hydroboration of styrene using (S)-Ipc_2BH:

PhCH=CH2+(S)-Ipc2BH→PhCH(BH2)CH3→PhCH(OH)CH3

1. **Formation of the Borane-Alkene Complex**: Styrene forms a complex with (S)-Ipc_2BH, aligning such that the steric bulk of the isopinocampheyl groups dictates the approach of the alkene.
2. **Syn Addition**: The boron atom and a hydrogen atom add to the same face of the double bond in styrene, forming a chiral organoborane intermediate.
3. **Oxidative Workup**: The intermediate is oxidized using H_2O_2 and NaOH, resulting in (S)-1-phenylethanol with high enantioselectivity.

   Complex Formation: PhCH=CH2+(S)-Ipc2BH→PhCH(BH2)CH3

Oxidative Workup:

The resulting alcohol, (S)-1-phenylethanol, is obtained with high enantioselectivity due to the influence of the (S)-Ipc_2BH reagent.

PhCH(BH2)CH3+H2O2/NaOH→PhCH(OH)CH3

Chiral catalyst controlled asymmetric synthesis:

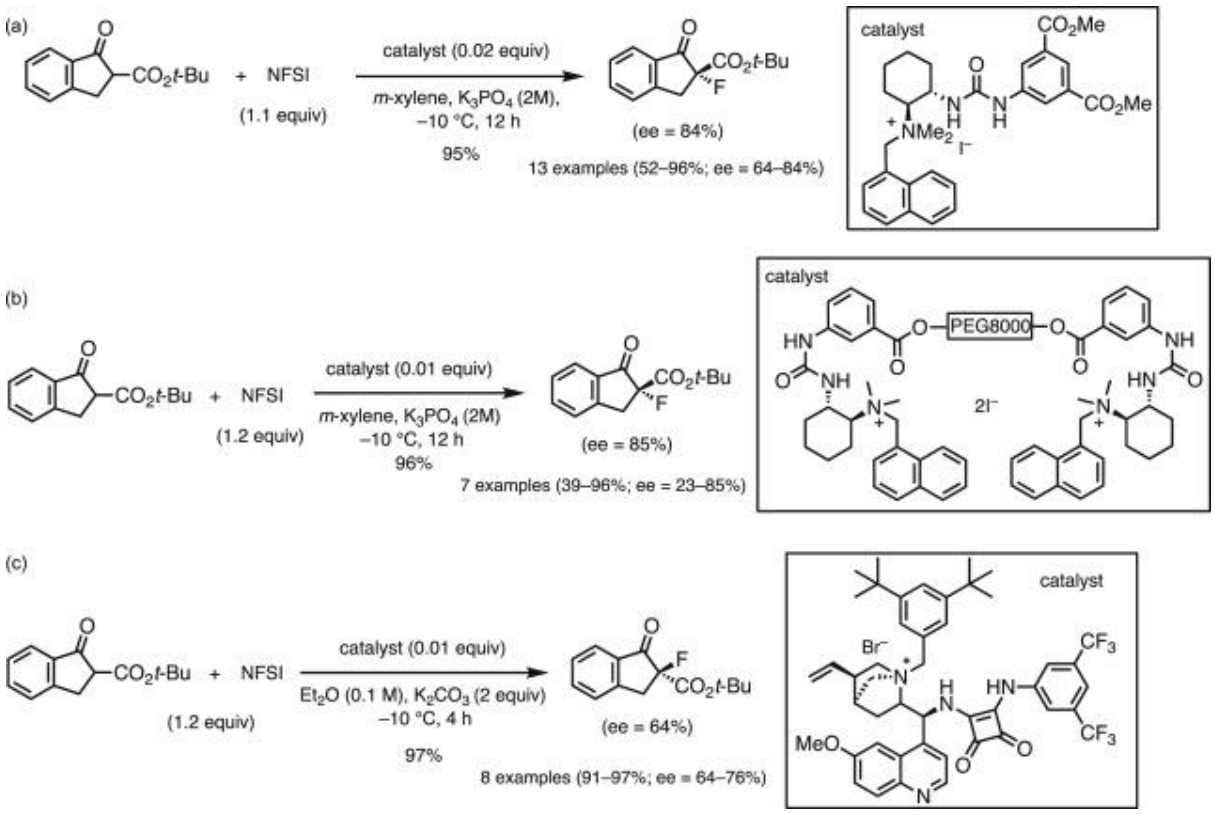
The chiral catalyst can provide chiral environment,it is required for enantioselective reaction.

The quantity of chiral catalyst is used in very small amount (5-10 moles) .

These 5-10 moles converts 100achiral molecules into 100 chiral moles.

In Asymmetric reaction,Chiral catalysts or enzymes are responsible for unequal ratio of formation of products.

Ex:Jacobson catalyst is used for the asymmetric epoxidation of simple olefins.



Sharpless epoxidation is a widely used method for the enantioselective synthesis of epoxides from allylic alcohols. Developed by K. Barry Sharpless, who was awarded the Nobel Prize in Chemistry in 2001, this reaction utilizes a chiral catalyst to induce enantioselectivity, making it a corner stone in asymmetric synthesis.

Key Features

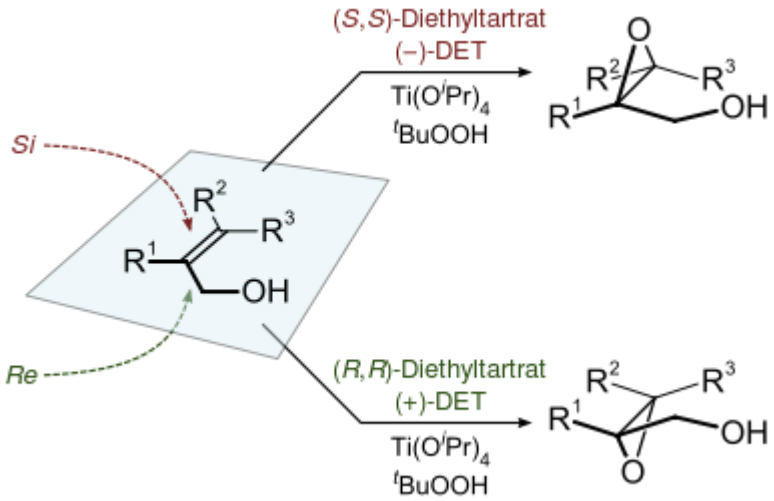
1. **Substrates**: Primarily allylic alcohols.
2. **Catalyst**: Chiral titanium-tartrate complex.
3. **Oxidizing Agent**: tert-Butyl hydroperoxide (TBHP).
4. **Enantioselectivity**: High, controlled by the chiral tartrate ester.

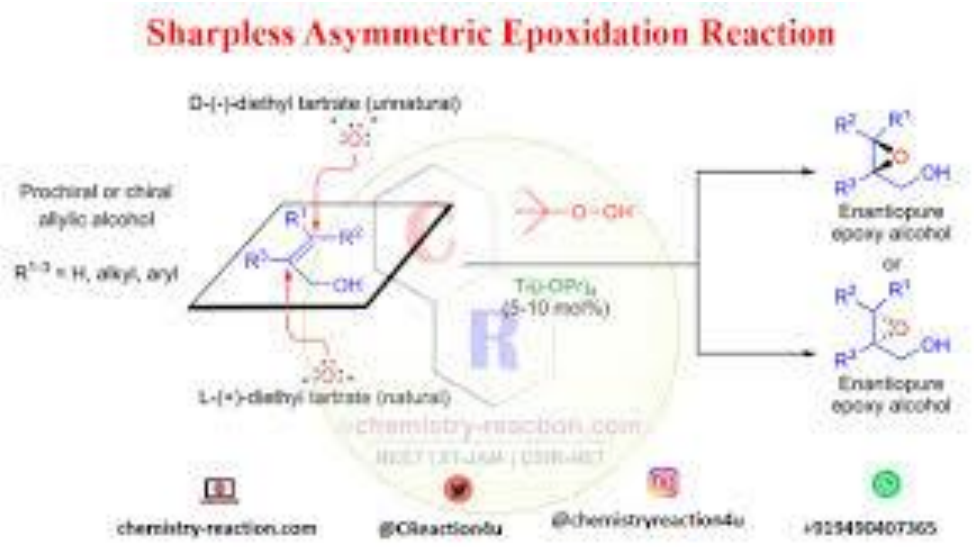
General Reaction

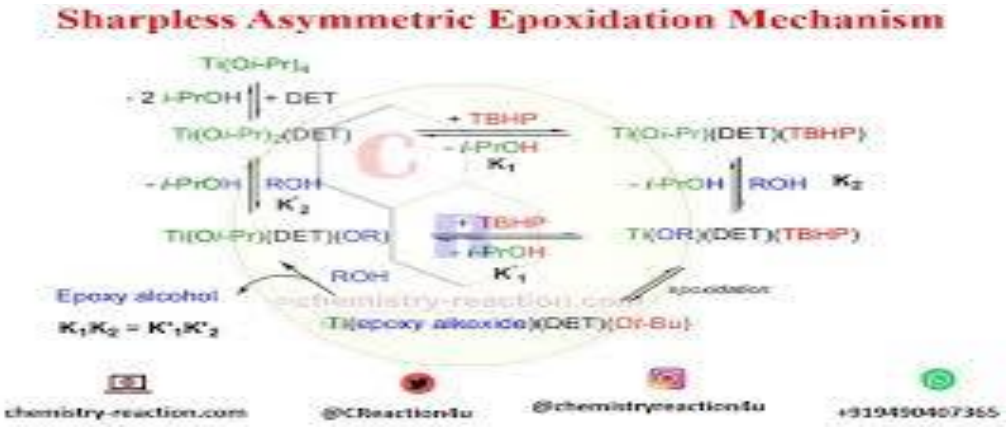
Allylic Alcohol+TBHP+Chiral Ti-Tartrate Catalyst→Chiral Epoxide

Mechanism

1. **Formation of the Chiral Catalyst Complex**:
    - The titanium(IV) isopropoxide reacts with the chiral tartrate ester to form the chiral catalyst complex.
    - The tartrate ester is typically either diethyl tartrate (DET) or diisopropyl tartrate (DIPT).







2. **Coordination of the Allylic Alcohol**:
    - The allylic alcohol coordinates to the titanium center of the chiral catalyst complex.
3. **Epoxidation**:
    - The oxidizing agent, TBHP, is introduced, leading to the formation of the epoxide ring on the allylic alcohol.
    - The chirality of the tartrate ester induces enantioselectivity in the epoxidation.

Enantioselectivity Control

- **(R,R)-DET**: Produces the (R)-epoxide.
- **(S,S)-DET**: Produces the (S)-epoxide.

Example Reaction

Consider the epoxidation of (E)-2-hexen-1-ol using (R,R)-diethyl tartrate (DET):

1. **Formation of the Chiral Catalyst Complex**:
2. **Coordination and Epoxidation**:

Applications

- **Pharmaceuticals**: Synthesis of chiral drug intermediates.
- **Natural Products**: Construction of complex natural products with high enantiomeric purity.
- **Agrochemicals**: Synthesis of chiral agrochemicals for specific biological activities.

Advantages

- **High Enantioselectivity**: The Sharpless epoxidation typically offers excellent enantioselectivity.
- **Mild Conditions**: The reaction conditions are generally mild, making it compatible with various functional groups.
- **Scalability**: The reaction can be scaled up for industrial applications.

Jacobsen's asymmetric dihydroxylation is a widely used method for the enantioselective synthesis of vicinal diols from alkenes. Developed by Eric Jacobsen, this reaction uses a chiral manganese(III) salen complex as a catalyst to achieve high enantioselectivity. The method is highly valuable in organic synthesis for its ability to convert simple alkenes into complex, chiral diols.

Key Features

1. **Substrates**: Typically alkenes.
2. **Catalyst**: Chiral manganese(III) salen complex.
3. **Oxidizing Agent**: Sodium hypochlorite (NaOCl) or other suitable oxidants.
4. **Enantioselectivity**: High, controlled by the chiral salen ligand.

General Reaction

$$\text{Alkene} + \text{NaOCl} + \text{Chiral Mn(III) Salen Catalyst} \rightarrow \text{Chiral Vicinal Diol}$$

Mechanism

1. **Formation of the Chiral Catalyst Complex**:
    - The chiral manganese(III) salen complex is prepared from the corresponding salen ligand and a manganese salt.
    - The chiral ligand is typically synthesized from a diamine and a salicylaldehyde derivative.

2. **Coordination of the Alkene**:
    - The alkene coordinates to the manganese center of the chiral catalyst complex.
3. **Dihydroxylation**:
    - The oxidizing agent, often sodium hypochlorite (NaOCl), reacts with the manganese complex, forming a reactive manganese-oxo species.
    - The manganese-oxo species transfers an oxygen atom to the alkene, forming a cyclic intermediate.
    - Hydrolysis of the cyclic intermediate yields the chiral vicinal diol.

Enantioselectivity Control

- The chiral salen ligand induces enantioselectivity by controlling the approach of the alkene to the manganese-oxo species.

Example Reaction

Consider the asymmetric dihydroxylation of styrene using a chiral Mn(III) salen complex:

Styrene+NaOCl+Chiral Mn(III) Salen Catalyst→(R,R)-1,2-Phenylethanediol

1. **Formation of the Chiral Catalyst Complex**:
2. Chiral Salen Ligand+Mn(III) Salt→Chiral Mn(III) Salen Complex

3. **Coordination and Dihydroxylation**:

   Chiral Mn(III) Salen Complex+Styrene+NaOCl→

   (R,R)-1,2-Phenylethanediol

Applications

- **Pharmaceuticals**: Synthesis of chiral diols, which are important intermediates in the production of various pharmaceuticals.
- **Natural Products**: Construction of complex natural products with high enantiomeric purity.
- **Agrochemicals**: Synthesis of chiral agrochemicals for specific biological activities.

Advantages

- **High Enantioselectivity**: Jacobsen's dihydroxylation typically offers excellent enantioselectivity.
- **Mild Conditions**: The reaction conditions are generally mild, making it compatible with various functional groups.
- **Broad Substrate Scope**: The method can be applied to a wide range of alkenes.

Limitations

- **Substrate Specificity**: The reaction works best with certain types of alkenes.
- **Catalyst Sensitivity**: The chiral catalyst complex can be sensitive to air and moisture.

UNIT –III PHOTOCHEMISTRY

Photochemistry is the study of the interaction of electromagnetic radiation with matter resulting into a physical change or into a chemical reaction.

Primary Processes One molecule is excited into an electronically excited state byν absorption of a photon, it can undergo a number of different primary processes.

Photochemical processes are those in which the excitedν species dissociates, isomerizes, rearranges, or react with another molecule.

Photo physical processes include radiative transitions in whichν the excited molecule emits light in the form of fluorescence or phosphorescence and returns to the ground state, and intramolecular non-radiative transitions in which some or all of the energy of the absorbed photon is ultimately converted to heat.

Laws Governing Absorption Of Light Lambert's Law: This law states that decrease in the intensity of monochromatic light with the thickness of the absorbing medium is proportional to the intensity of incident light.

$$-dI/dx \propto I \quad -dI/dx=KI,$$

on integration changes to $I=I0\ e^{-Kx}$

Where , I0 = intensity of incident light.

I=intensity of transmitted light.

K= absorption coefficient.

Beer's Law : It states that decrease in the intensity of monochromatic light with the thickness of the solution is not only proportional to the intensity of the incident light but also to the concentration 'c' of the solution.

Mathematically, $-dI/dx \propto Ic \quad -dI/dx = \epsilon Ic$

on integration $I=I0\ e^{-\epsilon CX}$

Where, ϵ = molar absorption coefficient or molar extinction coefficient
Numerical value of Einstein

In CGS Unitsν $E=2.86/\lambda(cm)$ cal per mole or $=2.86X105 / \lambda(A0)$ K cal per mole

In SI units♣ E=0.1197/λ(m)J mol -1

GrotthuSs-Draper Law(First Law of Photochemistry): Only the light which is absorbed by a molecule can be effective in producing photochemical changes in the molecule.

Stark-Einstein's Law (Second Law of Photochemistry): It states that for each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction. The energy absorbed by one mole of the reacting molecules is E=Nhv. This energy is called one einstein. Or

E =11.97X10-5 /λ(m)KJ mol-1

Processes of photochemical reactions

1. Primary Process: Atoms or molecules activated by actual absorption of radiation. Or, the excitation of the species from the ground electronic state to excited state.

2. Secondary process: Activated species undergoes chemical reaction. ---Does not involve the absorption of light. Eg., Photochemical combination of Cl2 and H2 (It is chain mechanism)

a. Primary Process $2Cl. \rightarrow \nu Cl2 + h$ Chain Initiation step

Photochemical equivalence is applicable to this step

b. Secondary process Propagation reaction and Chain terminating step

Utility of the Laws

1. Calculation of the rates of formation of reactive intermediates in photochemical reactions

2. The study of the mechanisms of photochemical reaction

Quantum Yield (Φ): Quantum yield (Φ) is a measure of the efficiency of a photochemical reaction, which involves the conversion of absorbed photons into chemical products. For a reaction where HCl is involved, the quantum yield would indicate how efficiently light promotes a reaction that either consumes or produces HCl.

The quantum yield (Φ) is defined as the number of moles of product formed per mole of photons absorbed.

Mathematically, it can be expressed as:

Φ=Number of moles of product formed/Number of moles of photons absorbed
The hydrogen- chlorine reaction

We are considering the photolysis of Cl2 and H2
$2HCl(g)(radiation,\lambda=4800A0 \rightarrow H2(g) + Cl2(g)$)

Its quantum yield $=10^4$ to 10^6 ,because it is a chain reaction

Chain reaction : A chain reaction is one in which a single photo activated molecule sets off a sequence of reactions so that a very large number of reactant molecule react through a chain reaction.

Primary process, involve the decomposition of chlorine molecule into chlorine radicals. $2Cl \cdot \rightarrow \nu Cl2 + h$ (1) Chain Initiation step

In secondary process - propagate the chain by their continued reaction gives a large no. of HCl molecules.

Propagation reaction$\rightarrow$+ Cl2 Exothermic and low activation energy hence large no. of HCl molecule is formed before terminating the reaction. Hence the no of Cl2 molecules that undergoes reaction per each quantum of radiation absorbed is very large, ie, 104 to 106 . So the reaction has very high quantum yield. The chain is finally terminated by the combination of chlorine radicals on the walls of the vessels or in gas phase.

Cl2 (Chain terminating step)$\rightarrow Cl \cdot + Cl \cdot$

Photosensitization reactions: An electronically excited molecule can transfer its energy to a second species which then undergoes a photochemical process even though it was not itself directly excited.

eg, 1. Mercury acting as a photosensitizer: $Hg+hv \rightarrow Hg^*$

$$Hg^*+H2 \rightarrow H2^* + Hg$$

$$H2^* \rightarrow 2H \cdot$$

3. Chlorophyll acting as a photosensitizer :

Chlorophyll +hv → Chlorophyll *

6CO2+6H2O+ Chlorophyll *→ C6H12O6 + 6O2 + Chlorophyll

3 Chlorine photosenstizes the reaction of ozone to oxygen.

Cl2 +hv →Cl2 *

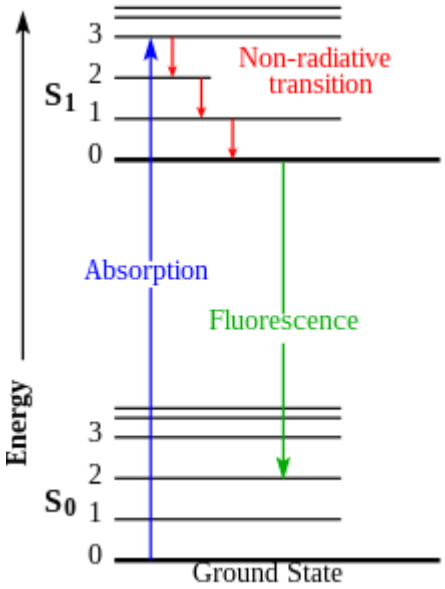
Cl2* + O3 → Cl2 + O2+ O

O+O3 →2O2

Luminescence The glow produced in the body by methods other than action of heat i.e. the production of cold light is called Luminescence. It is of three types,

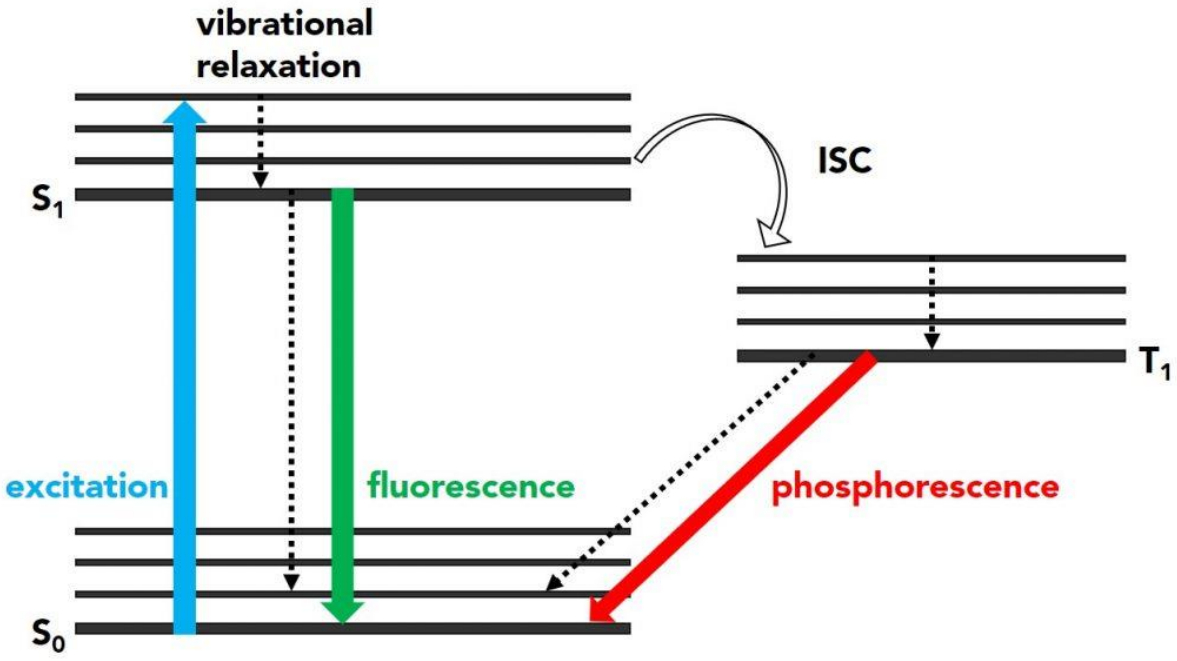
1. Chemiluminescence: The emission of light in chemical reaction at ordinary temperature is called Chemiluminescence e.g. The light emitted by glow-worms

2. Fluorescence: Certain substances when exposed to light or certain other radiations absorb the energy and then immediately start re-emitting the energy. Such substances are called fluorescent substances and the phenomenon is called fluorescence . e.g Organic dyes such as eosin,fluorescein etc. vapour of sodium,mercury,iodine etc.



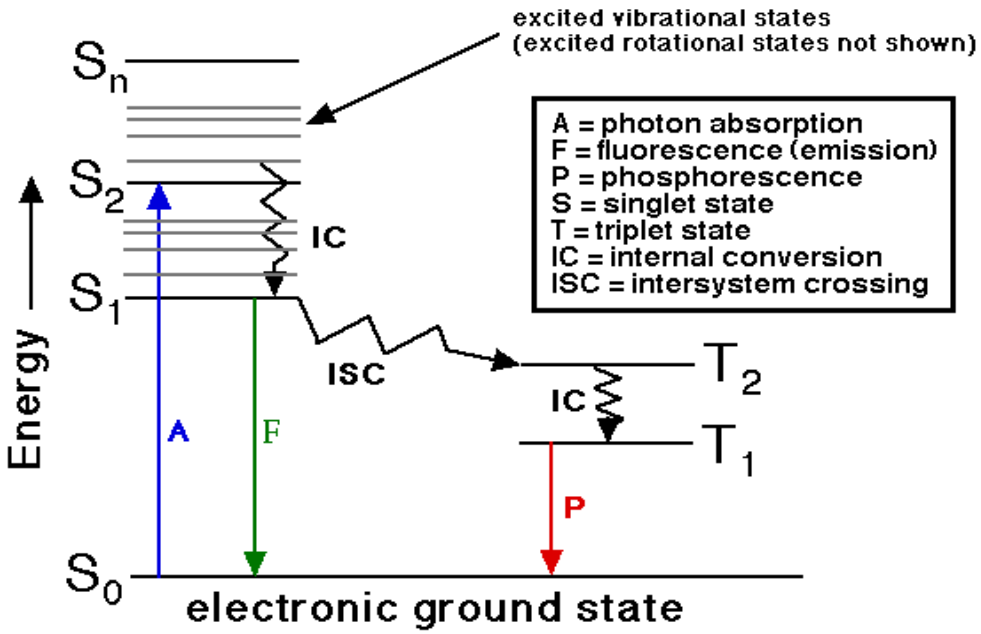
4. **Phosphorescence:** There are certain substances which continue to glow for some time even after the external light is cut off. Thus, phosphorescence is a slow fluorescence. Fluorescence and phosphorescence in terms of excitation of electrons Singlet ground Singlet excited state S1 Triplet excited state T1 state So (pair of electrons with (pair of electrons with Opposite spins but each parallel spins in

different Orbital's) in different orbital) The excited species can return to the ground state by losing all of its excess energy by any one of the paths shown in Jablonski diagram.



Jablonski diagram.

Jablonski Diagram for various photophysical processes Allowed singlet states: Forbidden triplet states due to spin conversion.



Explanation of Jablonski Diagram

First step: is the transition from higher excited singlet states (S2, S3, …) to the lowest excited singlet state S1.This is called internal conversion (IC). It is a non-radiative process and occurs in less than 10-11 second. Now from S1 the molecule returns to ground state by any of the following paths.

Path I : The molecule may lose rest of the energy also in the form of heat so that the complete path is non-radiative or radiation less transitions.

Path II: Molecule releases energy in the form of light or uv radiation. This is called Fluorescence

Path III : Some energy may be lost in transfer from S1 to T1 in the form of heat. It is called intersystem crossing (ISC). This process involves transition between states of different spins (parallel to antiparallel), ie, different multiplicity. This path is non-radiative.

Path IV : After ISC, the molecule may lose energy in the form of light in going from the excited triplet state to the ground state. This is called phosphorescence. Chemical reaction The activated molecule loses energy by undergoing chemical reaction. Since the molecules in singlet excited sates returns quickly to the G.S, it gets no chance to react chemically. However the molecules in the triplet state returns to the G.S. slowly, has a opportunity to the activated molecule undergoes chemical reaction. i.e., the molecule which undergoes chemical reaction is one which is previously present in a triplet state.

NORRISH TYPE-I REACTION:

The Norrish Type I reaction is a photochemical cleavage reaction that involves the homolytic cleavage of a carbon-carbon bond adjacent to a carbonyl group in a molecule upon exposure to UV light. This reaction is particularly important in organic chemistry for generating radical intermediates, which can then participate in various rearrangements or reactions.

Mechanism Overview:

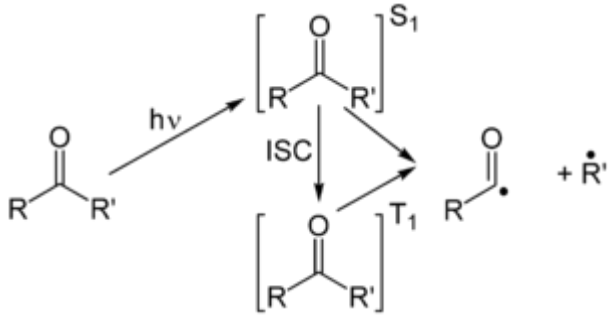
1. **Excitation**: The molecule absorbs UV light, promoting an electron from the ground state to an excited state. This excitation often involves a π-electron of the carbonyl group.
2. **Formation of Excited State**: The molecule reaches an excited singlet state (S1)(S_1)(S1) or triplet state (T1)(T_1)(T1) upon absorbing light.

3. **Homolytic Cleavage**: The excited state undergoes homolytic cleavage of a bond adjacent to the carbonyl group, resulting in the formation of two radicals.
4. **Radical Formation**: This cleavage produces two radicals: one on the carbonyl carbon and one on the adjacent carbon. The nature of these radicals depends on the specific structure of the molecule.
5. **Reaction of Radicals**: The radicals formed can then undergo various reactions, such as radical-radical coupling, radical rearrangements, or reactions with other molecules.

Example Reaction:

An example of the Norrish Type I reaction involves acetone CH_3COCH_3

1. **Starting Material**: Acetone
2. **Excitation**: Acetone absorbs UV light, promoting an electron from the π-system around the carbonyl group to an excited state.
3. **Cleavage**: The excited acetone molecule undergoes homolytic cleavage of the carbon-carbon bond adjacent to the carbonyl group.
4. **Formation of Radicals**: This cleavage produces two radicals:
    - Acetyl radical $CH_3CO\cdot$
    - Methyl radical $\cdot CH_3$
5. **Reaction Products**: These radicals can react further to form products such as methane and carbon monoxide, among others, depending on the conditions and other factors present.



Norrish Type II reaction

The Norrish Type II reaction is a photochemical cleavage reaction that involves the homolytic cleavage of a carbon-carbon bond adjacent to a carbonyl group in a molecule upon exposure to UV light. This reaction is characterized by the formation of a biradical intermediate, which subsequently undergoes rearrangement or reaction to form new products.

Mechanism Overview:

1. **Excitation**: The molecule absorbs UV light, promoting an electron from the ground state to an excited state. This excitation typically involves π-electrons of the molecule.
2. **Formation of Excited State**: The molecule reaches an excited singlet state (S1)(S_1)(S1) or triplet state (T1)(T_1)(T1) upon absorbing light.
3. **Bond Cleavage**: The excited state undergoes homolytic cleavage of a carbon-carbon bond adjacent to a carbonyl group. Unlike Norrish Type I, in Type II reactions, this bond cleavage occurs across the carbonyl group, leading to the formation of a biradical intermediate.
4. **Formation of Biradical Intermediate**: The cleavage produces two radicals:
    - A carbonyl radical (typically an acyl radical) and
    - A γ-radical (a radical at the carbon three positions away from the carbonyl carbon).
5. **Rearrangement**: The biradical intermediate undergoes rearrangement or reaction to form new products. This step often involves intramolecular rearrangements, such as shifts of double bonds or hydrogen migrations.
6. **Product Formation**: The rearranged intermediates eventually lead to the formation of final products, which can be different from the starting material.

Example Reaction:

An example of the Norrish Type II reaction involves the photochemical decomposition of benzophenone:

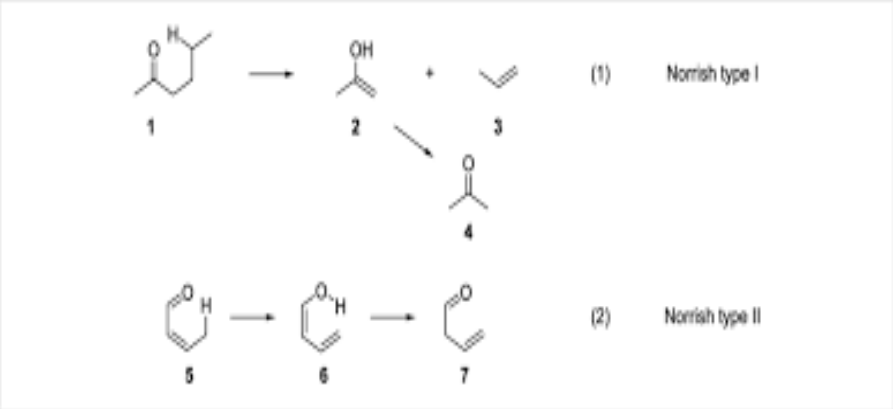
1. **Starting Material**: Benzophenone (C6H5COPh)
2. **Excitation**: Benzophenone absorbs UV light, promoting an electron from the π-system around the carbonyl group to an excited state.
3. **Cleavage**: The excited benzophenone molecule undergoes homolytic cleavage of the carbon-carbon bond adjacent to the carbonyl group.
4. **Formation of Biradical Intermediate**: This cleavage produces:

    Benzoyl radical :C6H5CO·

    Phenyl radical :Ph·

1. **Rearrangement**: The benzoyl and phenyl radicals then undergo rearrangement. For example, the benzoyl radical may lose a hydrogen atom to form a benzoyl diradical, which can then rearrange to form products such as benzene and carbon monoxide.

2. **Product Formation**: The final products depend on the specific rearrangement pathways and conditions of the reaction.



Paternò-Büchi reaction

The Paternò-Büchi reaction is a photochemical reaction named after Italian chemists Giuseppe Paternò and Rinaldo Büchi. It involves the [2+2] cycloaddition of an excited carbonyl compound with an alkene or alkyne, resulting in the formation of cyclobutane derivatives. This reaction is particularly notable for its ability to form cyclic structures under mild conditions, facilitated by the absorption of UV or visible light.

Mechanism Overview:

1. **Excitation**: The carbonyl compound (such as ketones, aldehydes, or esters) absorbs UV or visible light, promoting an electron from the π-system of the carbonyl group to an excited state (S1S_1S1 or T1T_1T1).
2. **Formation of Excited State**: The excited carbonyl compound can then react with an alkene or alkyne in a [2+2] cycloaddition process. The alkene or alkyne acts as a dienophile in this reaction.
3. **Cycloaddition**: The excited carbonyl compound and the alkene or alkyne undergo a concerted [2+2] cycloaddition reaction, leading to the formation of a cyclobutane ring.
4. **Product Formation**: The cyclobutane product is formed as a result of the cycloaddition. The reaction is typically regioselective and stereospecific, depending on the relative positions of substituents on the reacting partners.

Example Reaction:

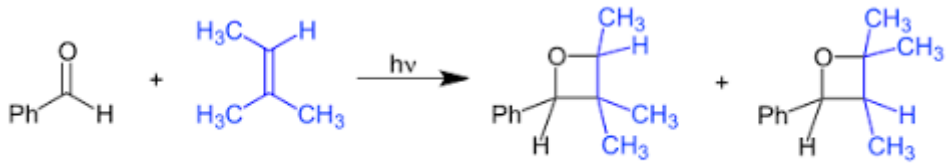
An example of the Paternò-Büchi reaction involves acetone and ethylene:

1. **Starting Materials**:

   Acetone (CH3COCH3)

   Ethylene (CH2=CH2)

2. **Excitation**: Acetone absorbs UV light, promoting an electron from its π-system to an excited state.
3. **Cycloaddition**: The excited acetone undergoes a [2+2] cycloaddition reaction with ethylene:
4. CH3COCH3∗+CH2=CH2→Cyclobutane derivative
5. **Product**: The product of this reaction is a cyclobutane derivative resulting from the [2+2] cycloaddition of acetone and ethylene.



2a **2b**

UNIT-4 PHOTOCHEMISTRY-II

DI-Π-METHANE REARRANGEMENT

The di-π-methane rearrangement is a photochemical reaction that involves the rearrangement of certain alkenes or dienes upon exposure to ultraviolet (UV) light. This rearrangement leads to the formation of cyclopropane derivatives. The name "di-π-methane" refers to the involvement of two π-systems (double bonds) and a methylene (CH_2) group in the rearrangement process.

Key Features

1. **Substrates**: Typically, the substrates are alkenes, dienes, or allyl-substituted aromatic compounds that have the structure where two π-systems are separated by a methylene group.
2. **Activation**: UV light is used to initiate the reaction.
3. **Product**: The reaction results in the formation of a cyclopropane derivative.

Mechanism

The mechanism of the di-π-methane rearrangement involves several key steps:

1. **Photoexcitation**: The substrate absorbs UV light, which promotes it to an excited state (usually a singlet or triplet state).
2. **Intramolecular Interaction**: In the excited state, there is an intramolecular interaction between the two π-systems and the methylene group.
3. **Formation of a 1,4-Biradical**: The interaction leads to the formation of a 1,4-biradical intermediate.
4. **Rearrangement**: The 1,4-biradical undergoes a rearrangement to form a new bond between the central carbon of the methylene group and one of the carbons of the π-systems, resulting in a cyclopropane ring.

Example Reaction

Consider the rearrangement of 1,1,6-trimethyl-1,4-hexadiene:

1. 1,1,6-Trimethyl-1,4-hexadienehv3,3,6-Trimethyl-1,4-hexadiene
2. **Photoexcitation**: UV light excites the diene.
3. **Intramolecular Interaction**: The excited state allows interaction between the double bonds and the methylene group.
4. **Formation of 1,4-Biradical**: The interaction forms a 1,4-biradical intermediate.

5. **Rearrangement to Cyclopropane**: The biradical rearranges to form a cyclopropane derivative.

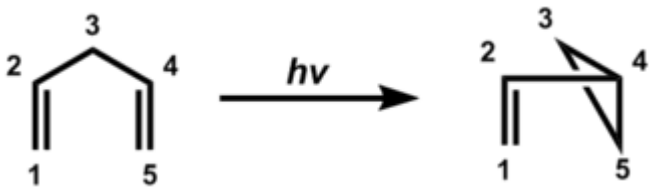


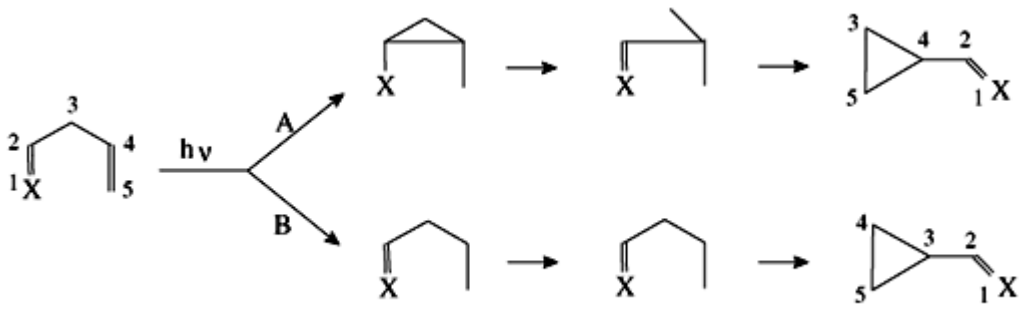
Diagram of the Mechanism

1. **Photoexcitation**: R-CH=CH-CH2-CH=CH-R hv(Excited State)
2. **Formation of 1,4-Biradical**:

   (Excited State)→·R-CH-CH···CH-CH=CH-R·

Rearrangement to Cyclopropane:

·R-CH-CH···CH-CH=CH-R·→Cyclopropane Derivative



Scheme 2.

Applications

- **Synthesis of Cyclopropanes**: Cyclopropanes are valuable intermediates in organic synthesis and pharmaceuticals.
- **Study of Photochemical Reactions**: The di-π-methane rearrangement serves as a model for understanding the behavior of excited states and biradical intermediates.

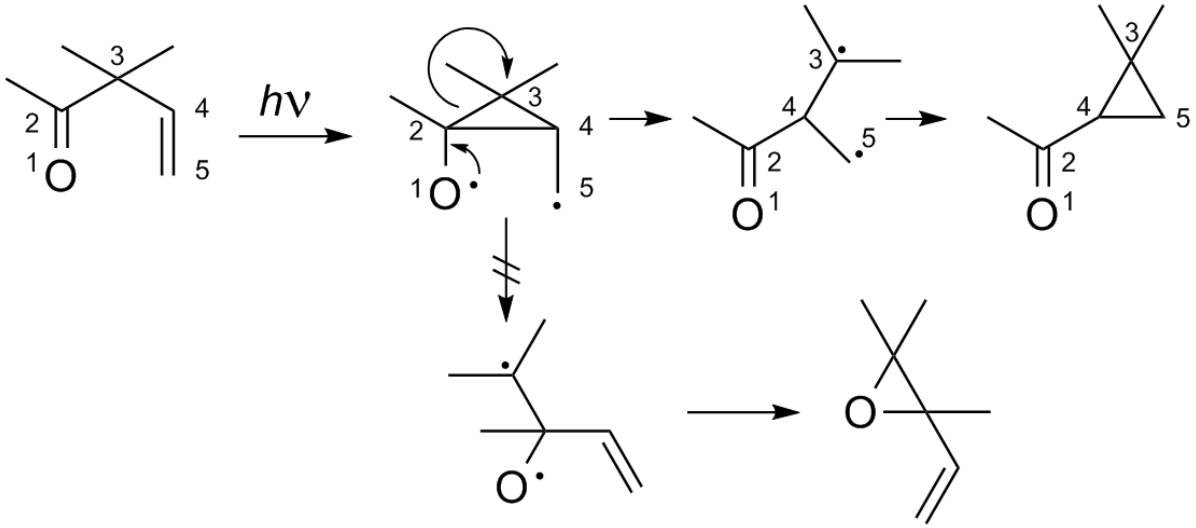
OXA-DI-Π-METHANE REARRANGEMENT

The oxa-di-π-methane rearrangement is a photochemical reaction similar to the di-π-methane rearrangement, but it involves substrates where one of the π-systems is an oxygen-containing group, such as an alkene conjugated with an aldehyde or a ketone (carbonyl group). This reaction leads to the formation of

products where a new carbon-oxygen bond is formed, often resulting in cyclopropanol or related structures.

Key Features

1. **Substrates**: Typically, the substrates are enones or similar compounds where a double bond is conjugated with a carbonyl group (C=O).
2. **Activation**: UV light is used to initiate the reaction.
3. **Product**: The reaction typically forms cyclopropanol derivatives or other oxygen-containing cyclic compounds.



Mechanism

The mechanism of the oxa-di-π-methane rearrangement involves several key steps:

1. **Photoexcitation**: The substrate absorbs UV light, which promotes it to an excited state, usually a triplet state.
2. **Intramolecular Interaction**: In the excited state, there is an intramolecular interaction between the π-system of the double bond and the π-system of the carbonyl group.
3. **Formation of a 1,4-Biradical**: The interaction leads to the formation of a 1,4-biradical intermediate.
4. **Rearrangement**: The 1,4-biradical undergoes a rearrangement to form a new bond between the central carbon of the methylene group and the oxygen, resulting in a cyclopropanol or related structure.

Example Reaction

Consider the rearrangement of 3-hexen-2-one:

3-Hexen-2-one $\xrightarrow{h\nu}$ 2-Ethyl-2,3-epoxybutane

Photoexcitation: UV light excites 3-hexen-2-one.

1. **Intramolecular Interaction**: The excited state allows interaction between the double bond and the carbonyl group.
2. **Formation of 1,4-Biradical**: The interaction forms a 1,4-biradical intermediate.
3. **Rearrangement to Cyclopropanol**: The biradical rearranges to form a cyclopropanol derivative.

Mechanism

1. **Photoexcitation**:

   R-CH=CH-CH=O$\rightarrow$hv (Excited State) R-CH=CH-CH=O

   Formation of 1,4-Biradical:

   (Excited State)$\rightarrow$·R-CH-CH···CH=O·

   Rearrangement to Cyclopropanol:

   ·R-CH-CH···CH=O·$\rightarrow$Cyclopropanol Derivative

Applications

- **Synthesis of Cyclopropanols**: Cyclopropanols and related structures are valuable intermediates in organic synthesis.
- **Study of Photochemical Reactions**: The oxa-di-π-methane rearrangement serves as a model for understanding the behavior of excited states and biradical intermediates involving oxygen.

Advantages

- **High Selectivity**: The reaction often proceeds with high regio- and stereoselectivity.
- **Mild Conditions**: As a photochemical process, it generally occurs under mild conditions without the need for strong reagents.

Limitations

- **Substrate Specificity**: The reaction is limited to substrates with appropriate π-systems conjugated with a carbonyl group.
- **Sensitivity to Conditions**: The reaction can be sensitive to the presence of oxygen and other quenching agents.

PHOTO-FRIES REARRANGEMENT

1. **Formation** The Photo-Fries rearrangement is a photochemical reaction that involves the migration of acyl groups in aryl esters upon exposure to ultraviolet (UV) light. This rearrangement results in the formation of ortho- and para-hydroxyaryl ketones. It is a valuable reaction in organic chemistry for modifying the structure of aromatic esters and is used to introduce functional groups at specific positions on the aromatic ring.

Key Features

1. **Substrates**: Aryl esters (Ar-COOR).
2. **Activation**: UV light is used to initiate the reaction.
3. **Products**: Ortho- and para-hydroxyaryl ketones (Ar-CO-Ar'OH).

Mechanism

The mechanism of the Photo-Fries rearrangement involves several key steps:

1. **Photoexcitation**: The aryl ester absorbs UV light, which promotes it to an excited singlet or triplet state.
2. **Cleavage**: In the excited state, the aryl ester undergoes homolytic cleavage of the C-O bond, forming an acyl radical (RCO·) and an aryl radical (ArO·).
3. **Radical Migration**: The acyl radical migrates to the ortho or para position of the aromatic ring.
4. **Recombination**: The aryl radical and the acyl radical recombine to form the ortho- and para-hydroxyaryl ketones.

Example Reaction

Consider the rearrangement of phenyl acetate (Ph-$COOCH_3$):

$$\text{Ph-COOCH3} \rightarrow \text{hv} \quad \text{PhCO-2-OHCH3} + \text{PhCO-4-OHCH3}$$

Photoexcitation: UV light excites phenyl acetate.

1. **Cleavage**: The excited state leads to the homolytic cleavage of the ester bond, forming phenoxy ($PhO\cdot$) and acetyl ($CH_3CO\cdot$) radicals.
2. **Radical Migration**: The acetyl radical migrates to the ortho and para positions of the aromatic ring.
3. **Recombination**: The radicals recombine to form ortho- and para-hydroxyacetophenone.

Diagram of the Mechanism

1. **Photoexcitation**:

$$Ph\text{-}COOCH3 \rightarrow hv(Excited\ State)Ph\text{-}COOCH3$$

2. **Cleavage**:

$$(Excited\ State)\ Ph\text{-}COOCH3 \rightarrow Ph\ CO\cdot + CH3CO\cdot$$

Radical Migration:

$$CH3CO\cdot \rightarrow ortho\text{- or para-position on the aromatic ring}$$

3. **Recombination**:

$$PhO\cdot + CH3CO\cdot \rightarrow ortho\text{- and para-hydroxyacetophenone}$$

Applications

- **Synthetic Organic Chemistry**: The Photo-Fries rearrangement is used to introduce functional groups at specific positions on aromatic rings.
- **Pharmaceuticals**: Synthesis of intermediates for drug development.
- **Material Science**: Modification of aromatic polymers and materials to introduce specific functionalities.

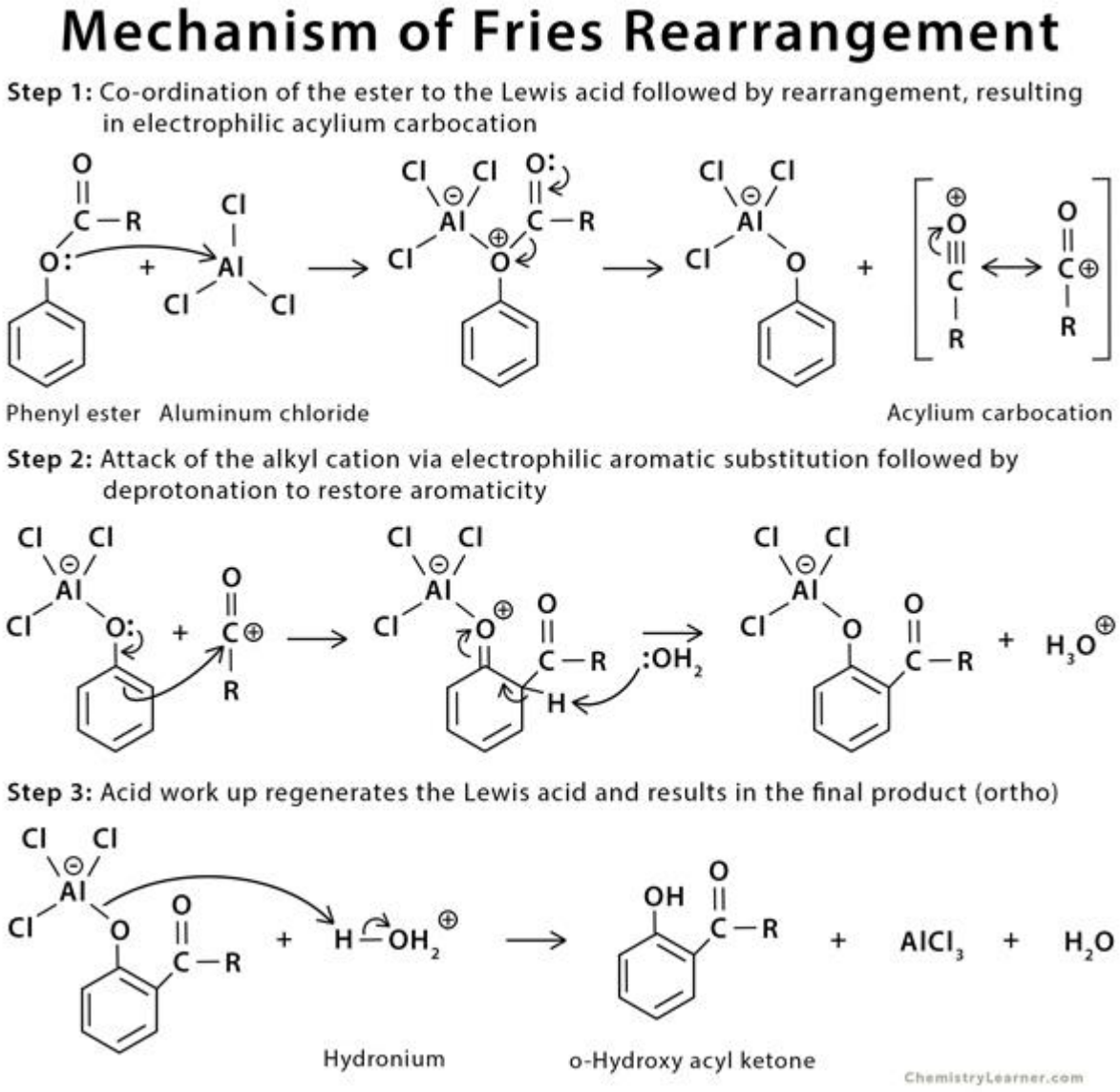
Advantages

- **Regioselectivity**: The reaction provides a method for selectively introducing acyl groups at the ortho and para positions of aromatic rings.
- **Mild Conditions**: The reaction can be performed under relatively mild conditions using UV light.

Limitations

- **Substrate Specificity**: The reaction is limited to aryl esters.

- **Control Over Product Distribution**: The ortho/para ratio can be difficult to control and may vary depending on the substrate and reaction conditions.



PHOTOCHEMICAL REARRANGEMENT OF CYCLOHEXADIENONE:

The photochemical rearrangement of cyclohexadienone is an interesting process that involves the transformation of a cyclohexadienone (often a 2,5-cyclohexadienone) into a phenol. This type of reaction is a specific example of a broader class of photochemical reactions where light energy causes a rearrangement of molecular structures.

Mechanism Overview:

1. **Excitation**: The cyclohexadienone absorbs UV light, promoting an electron from the ground state to an excited state. This usually involves the promotion of a π-electron to a π* orbital. leading to an excited singlet state (S1)(S_1)(S1)
2. **Intersystem Crossing (ISC)**: The excited singlet state can undergo intersystem crossing to form an excited triplet state, which is often more stable and reactive in this context.
3. **Norrish Type II Cleavage**: The excited state undergoes a Norrish Type II cleavage where a γ-hydrogen (a hydrogen three carbons away from the carbonyl group) is abstracted by the excited carbonyl oxygen, forming a biradical intermediate.
4. **Rearrangement**: The biradical intermediate undergoes a series of bond rearrangements and electron shifts, leading to the formation of a phenol.

Example Reaction:

For a specific example, consider the photochemical rearrangement of

2,5-cyclohexadienone to 4-hydroxy-2,5-cyclohexadienone:

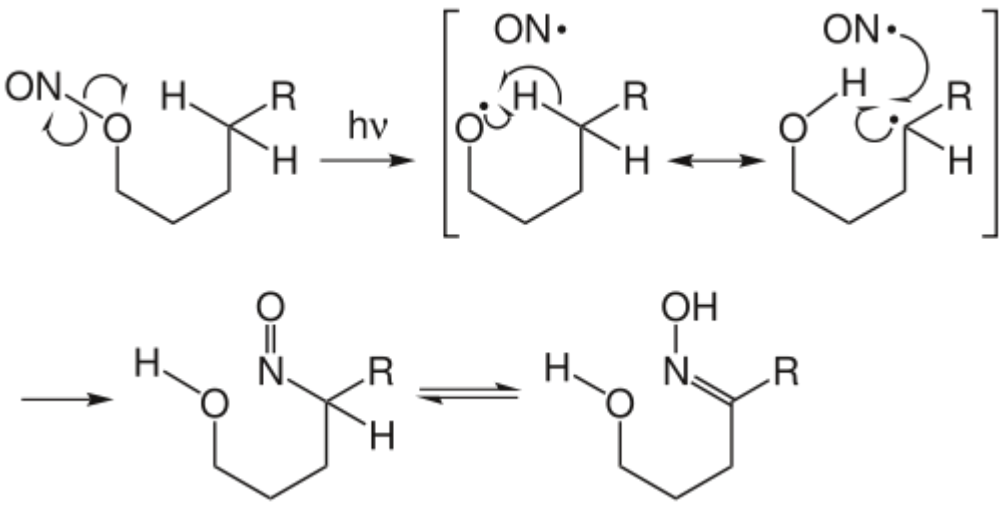
1. **Starting Material**: 2,5-Cyclohexadienone
2. **Product**: 4-Hydroxy-2,5-cyclohexadienone (Phenol derivative)

This process is significant in organic synthesis and can be used to synthesize various phenolic compounds from cyclohexadienone precursors. The key aspect of this reaction is the photochemical nature, where light energy facilitates the rearrangement, allowing for transformations that might be challenging under thermal conditions.

BARTON REACTION

The Barton nitrite ester photolysis (Barton reaction) is generally considered a landmark in the development of remote functionalizations. The reaction Involves the photolytic homolysis of a nitrite ester to generate an oxygen-centered radical that abstracts a hydrogen,usually from the δ-position.

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



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