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5. Green Chemistry Innovation and Technology

Vedant Patel, Kishor R. Desai,
Bhavin R. Patel

Tarsadia Institute of Chemical Science,
Uka Tarsadia University, Bardoli,
Tarsadi, Gujarat.

S. Ravichandran

Department of Chemistry,
School of Mechanical Engineering,
Lovely Professional university,
Jalandhar, Punjab, India.

Abstract:

Catalysis, or the use of catalysts to change the rate of a chemical process, dates back to the Neolithic era. Conventional catalysts can accelerate reaction rates without causing permanent changes, whereas biocatalysis uses enzymes to produce medications and chemicals. Biocatalytic techniques employ specialized precursor molecules and metabolizable carbon sources like sugars to efficiently produce functionalized products, even when non-natural substrates are used. Photochemical processes triggered by photons enable ecologically benign reactions with excellent selectivity and low temperatures. Still, they face problems such as fouling photochemical windows, inefficiencies caused by polychromatic light sources, and expensive equipment costs. Progress in reactor technology aims to overcome these limits and improve the viability of using photochemical processes in manufacturing environments.

Keywords:

Catalysis, biocatalysis, enzymes, photochemical processes

5.1 Introduction:

5.1.1 Biocatalysts:

- **Catalysts:** A small amount of Jo substance(s) introduced to a chemical process can change the rate of the reaction. Catalysis is the word used to describe this occurrence, while catalysts are the compounds used to change the rate of the reaction.[1] A catalyst is traditionally described as a material that increases the rate of a chemical reaction without experiencing irreversible chemical change after the process. Catalysis may be traced back to the Neolithic period, when biocatalytic fermentation was used to make wine, and animal fats were hydrolysed with potash lye to make soap. In 1836, the catalysis phenomenon first became scientifically recognized.[2]

Bio-catalysis utilizes enzymes' catalytic capacity to generate building blocks and end products for the pharmaceutical and chemical industries. Biotransformation processes, which exist at the intersection of fermentation and petroleum-based chemistry, expand the toolkit for the bioconversion of organic molecules into functionalized products.[3]

Biocatalytic processes follow a distinct strategy. Precursor molecules are supplied to the biocatalyst, which converts them to the desired chemical in a limited number of functionalizing steps (usually one). The carbon and energy necessary for biocatalyst manufacture are often derived from a separate, easily metabolizable carbon source, such as sugar.

The variety of products is not restricted by the biocatalyst's metabolism; non-natural (xenobiotic) precursor molecules can be successfully converted since biocatalysts can convert both natural and non-natural substances. The synthesis begins (more than) halfway along the pathway to the target molecule.[4]

5.1.2 Enzymes: The Key Elements for Biocatalysis:

Enzymes catalyze a large number of processes required for the production, modification, and destruction of the organic molecules that comprise living organisms. or that these creatures make in order to defend themselves and communicate. Metabolic pathways and cell development include a wide range of events, including the creation of carbon-carbon, peptide, and ester bonds, the saturation or desaturation of carbon-carbon bonds, and oxidation by, for example, oxygen. The corresponding enzymes have been grouped into six separate classes based on their catalytic characteristics.[5]

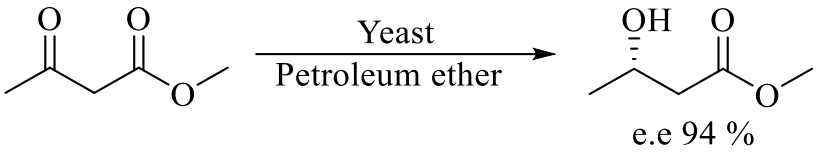
Oxidoreductases	-oxidation/reduction
Transferases	- transfer of functional groups
Hydrolases	- hydrolysis
Lyases	-addition/elimination of small molecules on sp^2-hybridized Carbon
Isomerases	- isomerization
Ligases	- formation/cleavage of sp^3-hybridized carbon[6]

Table 5.1: Advantages and disadvantages of biocatalysis in comparison with chemical catalysis[7]

Advantages	Disadvantages
Generally, more efficient (lower concentration of enzyme needed)	Susceptible to substrate or product inhibition
Can be modified to increase selectivity, stability, and activity	Solvent usually water (high boiling point and heat of vaporization)
More selective (types of selectivity: chemo-selectivity, regio-selectivity diastereo-selectivity, and enantio-selectivity)	Enzymes found in nature in only one enantiomeric form

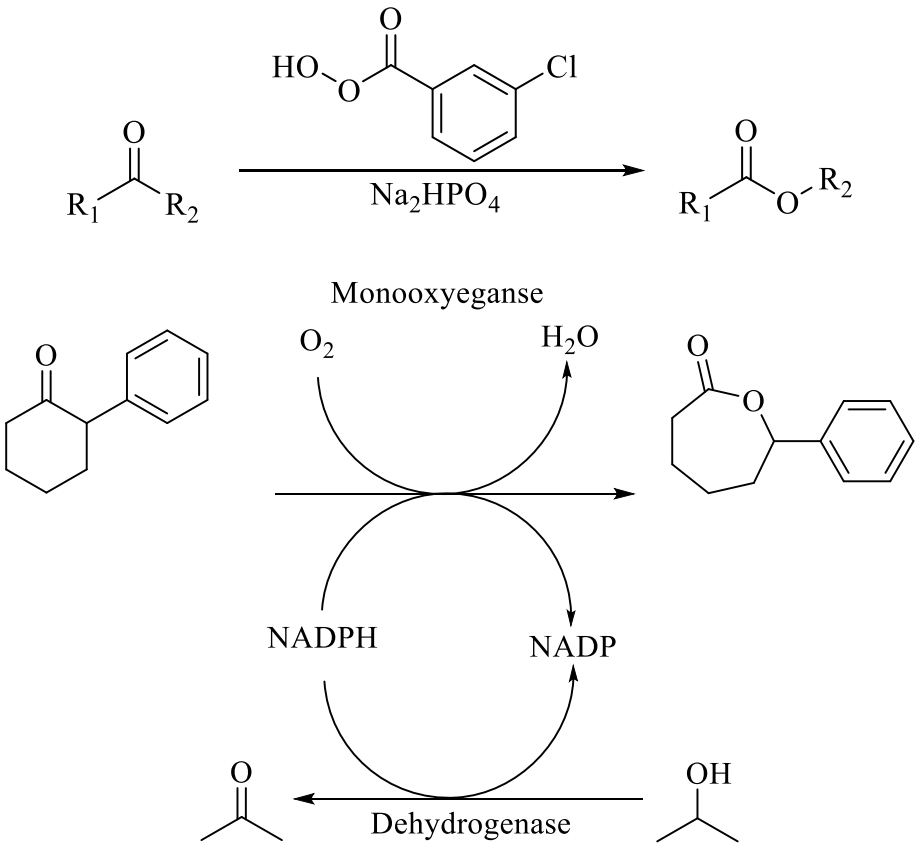
Advantages	Disadvantages
Milder reaction conditions (typically in L a pH range of 5-8 and temperature range of 20-40 C.	Limiting operating region (enzymes typically denatured at high temperature and pH)
Environment-friendly (completely degraded in the environment)	Enzymes can cause allergic reaction

Bio-catalyzed asymmetric synthesis for carbonyl compound[8]



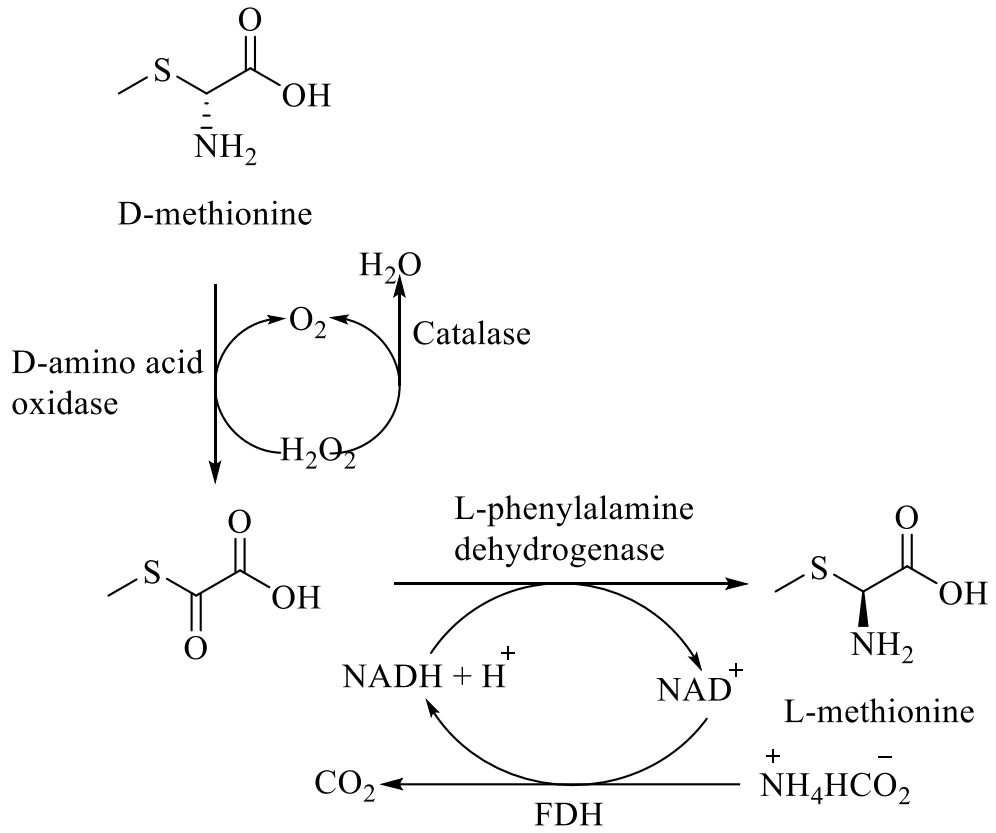
Yeast is a biocatalyst for the enantioselective reduction of ketones.

Bayer-Villiger Oxidation



Bayer-Villiger Monooxygenase or BVMO cofactors such as NADPH.[9]

Biocatalytic cascade for the deracemizations of methionine[10]



The Use of Biocatalysts for Green Chemistry:

Biocatalysis is the use catalysts derived from Nature to catalyse of chemical reactions. In this respect, developing countries could contribute enormously to achieving green chemistry principles by using their unique, diverse, and abundant natural resources to perform biotransformation This is however possible if effective and sustainable use of biological feedstock and generation of novel biocatalysts is achieved. Generally, the use of biotechnology gives enormous new innovative opportunities for green chemistry processes in industry. This is because biotechnology is growing at a very fast rate and it now represents a versatile and powerful technology towards achieving industrial green processes and products.[11]

Biocatalysis are capable of providing high selectivities (both stereo- and regio-) without using protection-deprotection groups and in this way., biocatalysts produce pure isomers as compared to racemic mixtures for non-biocatalysts.[12]

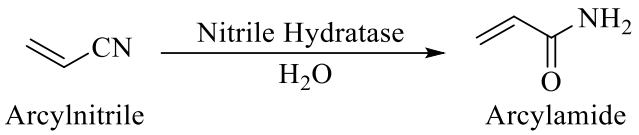
Generally, traditional downstream processes involve multi-step Processes and incur an overall increase in time, cost, energy, material, and waste disposal costs, which can be greatly reduced by the use of biocatalysis.[13]

At present, biocatalysts are important in the manufacture of intermediate, fine, and commodity chemicals, especially where enantio- and regio-selectivity are the key requirements.

The transformations involve either the use of a whole-cell enzyme or a partially purified enzyme Catalyst.

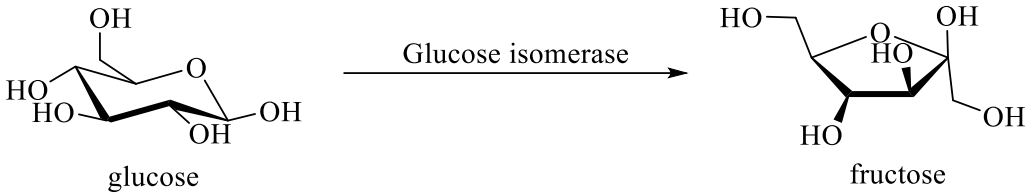
Although, industrial biotransformation is mainly on fine chemicals the industrial production of com-modity /bulk chemicals is also beginning to be common.

Mitsubishi Rayon is for instance using nitrile hydratase biocatalyst from *Rhodococus rhodochrous* to produce arylamide (scheme 1) on a scale of more than 30,000 tones per year.[14]

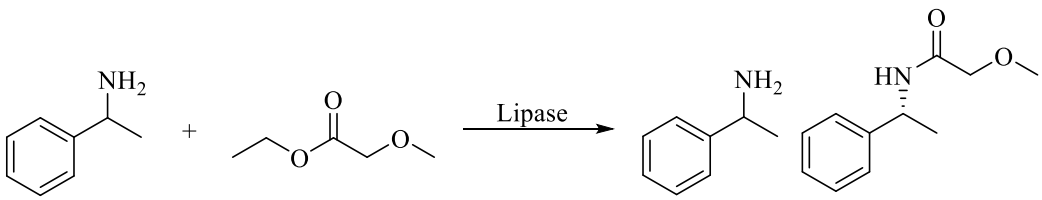


Scheme 1

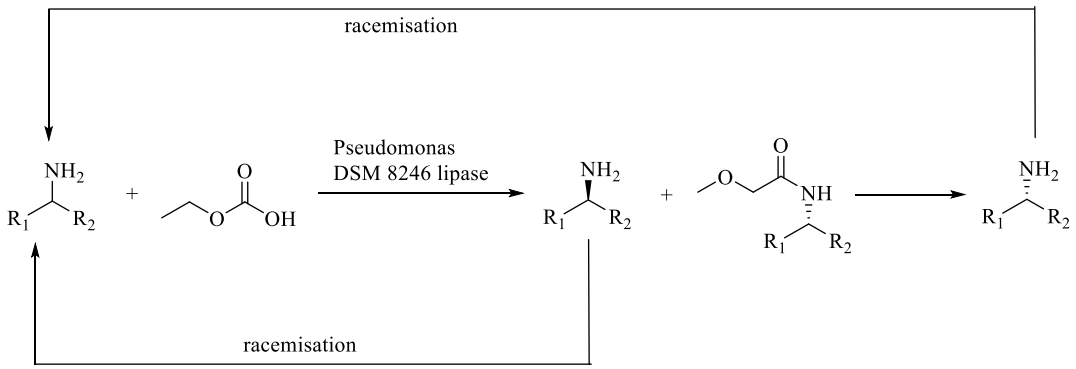
Another example of bio-catalysed (scheme 2) 1 is the production of fructose from glucose using glucose isomerase enzyme. About 100,000 tons of fructose per annum are produced by different companies through this production route.[12]

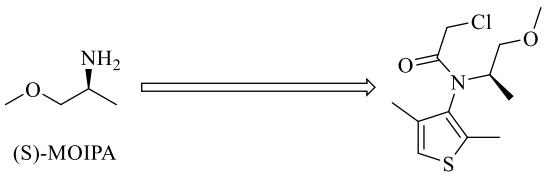


Biocatalytic resolution are hydrolases e.g., Lipases amidases, aminopeptidases, etc. A good example is BASF (Germany) that is industrially using *pseudomonas* lipase scheme 3 to get access to a broad range of enantiomerically pure (S) and (R) amines on a scale of about 100 tonnes per annum (. g (S)- phenylethylamine).[15]



BASF have used this biocatalytic route to industrially manufacture an agrochemical (FRONTIER X2R) of which only the (s)-enantiomer Se a biological activity (Scheme 4).[16]





(S)-MOIPA

FRONTER X2

Most of the bulk chemicals are presently manufactured by petroleum-phase hydrocarbons. New microbial production is considered an alternative process.

Advances in microbial genetics and understanding of metabolic pathways have let to the development of bacterial constructs with synthetic capabilities for converting sugars and other cheap raw materials to industrial chemicals and pharmaceuticals.

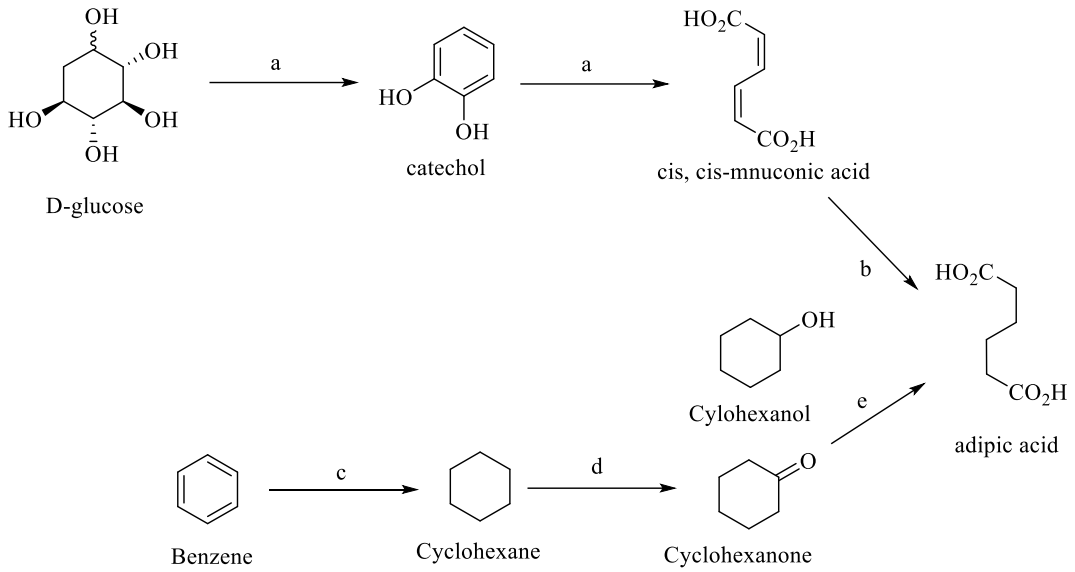
These biocatalytic processes not only offer advantages of higher production and cost saving but also result in reduced impact on the environment.[17] Molecular biology techniques are being used to evolve enzymes with better catalytic properties and stability as a result application of enzymes in various industries has tremendously increased.

At the existing pace of the Use of biocatalysts in industries, it is predicted that by the middle of the 21st century, biomass will supply 30% of the global market for energy and chemicals.[18]

Adipic acid S is used in the manufacture of Nylon-66. Annual global demand of more than 1.9×10^9 kg adipic acid is met by chemical synthesis as shown in Figure 5.1 in catechol synthesis, benzene from BTX fraction of petroleum is used as starting material.

Thus, this synthesis is also associated with environment-related problems. Reduction reaction requires very high temperature and pressure. Nitrous oxide is released during the nitric acid oxidation of cyclohexanone to adipic acid.

It is estimated that this synthesis alone contributes 10% of the annual increase in atmosphere N_2O levels. Nitrous oxide has been implicated in the reduction of stratosphere ozone levels as well as in global warming.[19, 20]

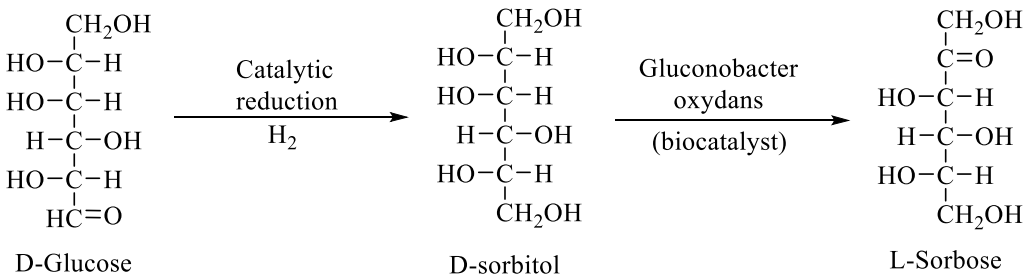


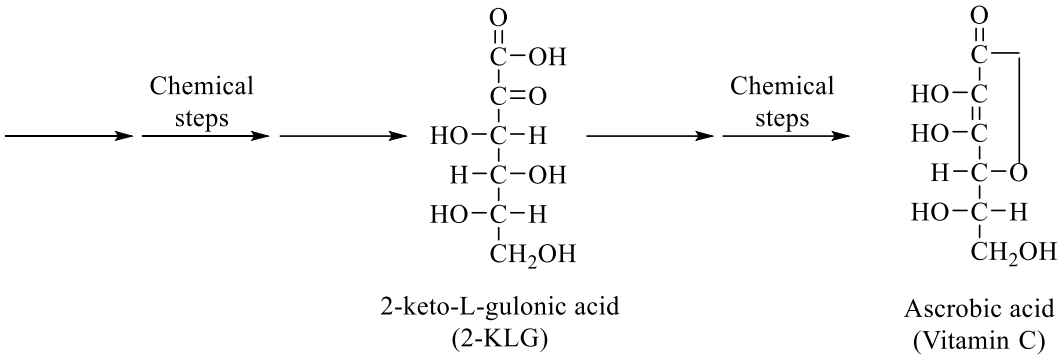
The synthesis of adipic acid. Glucose is converted to cis-cis muconic acid (Figure 5.1) using genetically engineered *E.coli* construct expressing the biosynthetic pathway which does not exist in nature.

The pathway was assembled by introducing the required genes for catechol 1,2 dioxygenase from *Acinetobacter calcoaceticus* to *E.coli* strain construct developed for the conversion of glucose to catechol mentioned earlier.[21]

Biocatalyst synthesized around 16.8 mM cis-cis- muconate from 56 mM glucose in a laboratory shake flask. After separating the bacterial cells, cis-cis muconate in the culture filtrate was directly reduced to adipic acid using platinum on carbon as catalyst at 50 psi for 3 hours at room temperature.[22]

Total world production of vitamin C exceeds 70,000 tons/year. it is currently manufactured by a Reichstein-Grussner synthesis (Fig 4.2) in which conversion of D-sorbitol to L-sorbose is a biotransformation step, where biocatalyst, *Gluconobacter oxydans* is used. L-sorbose is condensed with acetone to form sorbose diacetone, which is oxidized to 2-keto L gulonic acid (2-KLG). 2-KLG is then converted to L ascorbic acid.[23]





Few Frequently Use Microbial Biocatalysts:

Biocatalyst	% of total usage
Baker's yeast	30
Pseudomonas putida	11
Aspergillus niger	8
Beauveria bassiana, Beauveria sulfurescens, Sporotrichum sulfurescens, Cunninghamella elegans	5
Rhizopus nigricans, Rhizopus stolonifer	5
Curvularia lunata	4
Rhizopus arrhizus, Rhizopus oryzac	4
Cunninghamella echinulata	3.5
Mortierella isabellina	3

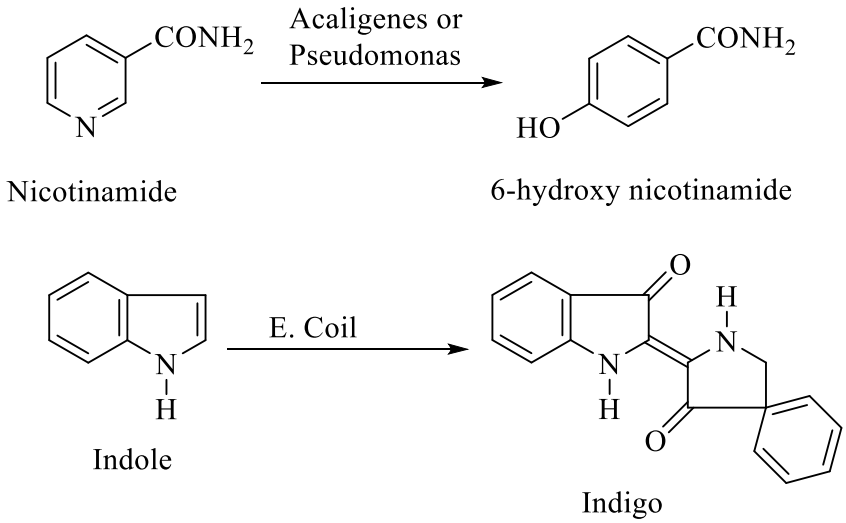


Figure 5.1: Commercially important biotransformation's without stereochemical features

Interest in green chemistry has led to the development of an alternate route for vitamin C synthesis. 2-KLG can be produced via 2,5- diketo-D gluconic acid (2-DKO) by a fermentation process using process using selected strains of *Erwinia herbicola* and *Corebacterium*. Another approach is to convert D-sorbitol or L-sorbose to 2-KLG via sorbosone. Recombinant strain developed to perform these reactions has been reported to produce 130g/1 of 2-KLG from 15% D-sorbitol based medium.[24]

Some typical reactions which are of commercial importance without stereochemical features are the conversion of acrylonitrile to acrylamide by *Rhodococcus rhodrockrous*, hydroxylation of nicotinic acid and related compounds at C_6 by *Pseudomonas* and the conversion of indole to indigo by *E.coli* expressing naphthalene dioxygenase gene (Figure 4.1)

These reactions represent "green" alternatives to conventional chemical procedures involving extreme conditions of temperature, pressure and/or harsh reagents. They represent the current emphasis placed on the development of environmentally acceptable industrial process.[25]

Vitamins:

Until recently, several vitamins, especially fat-soluble ones, and related compounds, were produced mainly either chemically or by extraction processes. However, microbiological production of these chemicals is now gaining wide attention.

Vitamins are generally synthesized by microorganisms in low concentrations. Production requires the development of hyper-producing microbial strains either by genetic manipulation or by r-DNA technology. The table gives the status of industrial production of a few vitamins.[26]

Table 5.2: Industrial Production of Vitamins[27]

Compound	Organic Chemistry	Extraction Chemistry	1	2	3	Word Production (tons/year)
Vitamin A	+			+		**2500**
Vitamin E	+				**(+)[a]**	**7000**
Vitamin F		+		+	**(+)[a]**	**100**
Vitamin K_2	+	+				**2**
Vitamin B_1	+		+			**2000**
Vitamin B_2	+		+	+		**>2000**
Vitamin B_6	+					**1600**
Vitamin B_{12}			+			**10**
Vitamin B_{13}			+			**100**
Vitamin C[b]	+		+			**>70,000**
Pantothenic acid	+		+			**4000**

*Parentheses indicate pilot scale process; 1 bacterial, 2 fungal, 3 algal

Compared to chemical synthesis, microbial processes offer several advantages. A part from obtaining these in a natural way, the end product is in the desired enantiomeric form, whereas products from chemical synthesis are often racemic mixtures. Further, they are environmentally benign.

Amino Acids:

Amino acids are the building blocks of proteins. Out of 20 amino acids present in proteins, all except glycine are L-enantiomers. Eight of these are essential for animals. There is a great demand for amino acids as they are used as food additives and also in the chemical industry such as in synthetic leather, surface active agents, fungicides, and pesticides.[28]

Production of Few Amino Acids Using Fermentation Process[29]

Amino Acid	Organism Used	Reported $yield_{max}$ in	Global annual fermentation broth	Major Uses Production
L-Glutamic acid	Corynebacterium glutamicum	150 g/l	1 million tons	Glavor enhancer in food industry
L-Lysine	Corynebacterium glutamicum	170 g/l	3,50,000 tons	Feed supplement
L-Threonine	E Coil	80 g/l	10,000 tons	Feed additive used for medicinal purposes

Another approach for amino acid production involves biotransformation using microbial enzymes. Asparatase is used to convert fumarate and ammonia to aspartic acid. Tryptophan, an essential amino acid can be synthesizes either from indole in the presence of biocatalyst tryphophanase or E Coil tryptophan synthase or form anthranilic acid.

Fermentation processes are usually simple and cheap. These processes may be, however, time-consuming. Furthermore, as a variety of compounds are formed during fermentation, extensive clean up procedures may be required.[29]

Precursors for enzymatic synthesis are in general more expensive, but the procedure is less time consuming and more efficient than fermentation method. However, it is expected that due to new procedures like metabolic engineering, which involves the improvement of cellular activities by manipulation of enzymatic transport and regulatory functions of the cell by the application of recombinant DNA technology, fermentation processes can become more cost-competitive.[30]

Biocatalytic synthesis of industrial chemicals by bacterial constructs:

Biocatalytic synthesis of catechol and adipic acid are classic examples of this approach. Catechol is the starting material for the synthesis of many pharmaceuticals, agrochemical,

antioxidants, flavours, etc. Worldwide production of catechol is around 21 million Kg^3. It is synthesized primarily from benzene, although a small prtion is distilled from coal tar.

Chemical synthesis if cethechol from benzene involves initial alkylation to cumene, which is then oxidizes to phenol. Phenol is further hydroxylated to yield a mixture of catechol and hydroquinone, which are then separated by distillation (fig. 4.4).[31]

This Chemical route of manufacture of catechol involves benzene, which is obtained form the benzene-toluene-xylene fraction of petroleum. Its supply thus depends on non-renewable feedstock. Benzene and phenol are toxic. The former is a known human carcinogen and the latter is listed as a priority pollutant by USEPA>H_2O_2 is a strong oxidant requiring special precautions for transportation, storage, and handling.[32]

To eliminate these environmental problems, attention is focussed on creating a microbial biocatalyst, which can convert glucose although it is formed as an intermediate during the degradation of a few aromatic compounds in bacteria and fungi that could not be manipulated. Instead, using molecular biology techniques, a novel biosynthetic pathway whose ultimate product is catechol was created.[33]

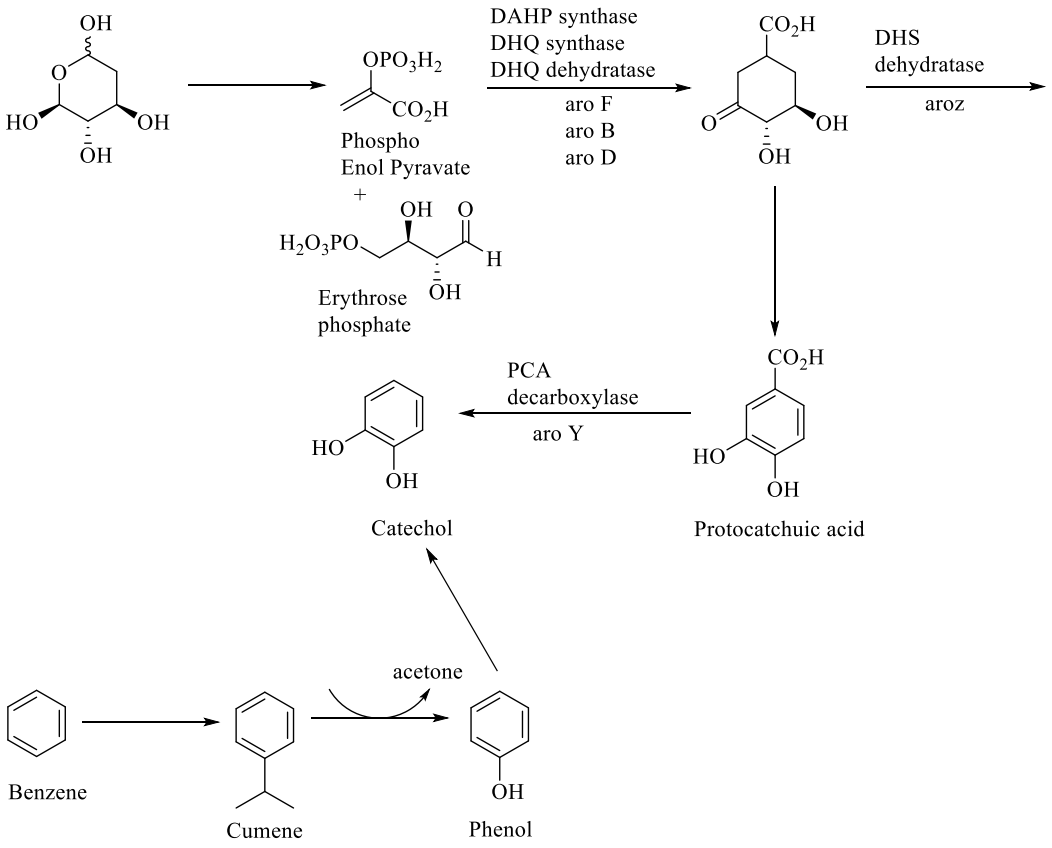


Figure 5.2 Chemical and Biocatalytic Pathway for catechol synthesis

Required enzymes for this pathway were expressed in the host organism *Escherchia coli* (Figure 5.2) after considering the following aspect (i) Maximizing the conversion of glucose to catechol is essential for biocatalytic catechol synthesis to be cost competitive with chemical process (ii) *E. Coli* Strains with maximum flow of organic carbon to the common pathway of aromatic acid biosynthesis were already available (iii) Catechol production requires the expression of genes for two enzymes, namely 3-dihydro shikimic acid dehydratase (DHS) and protocatechuic ○ decarboxylase which are absent in *E. Coli*.[34] The genes for these enzymes had to be isolated from different bacteria and expressed in a single host. Extensive work was available with *E. coil* for heterologous expression of enzymes. (iv) Another important consideration for choosing *E.coli* was the absence of catechol 1,2-oxygenase, in this organism. The presence of this enzyme and the associated degradation of catechol would decrease the accumulation of desired product.[35]

"Bacteria are capable of bringing about chemical reactions of amazing variety and subtlety in an extremely short time. Many bacteria are of great importance to industry, where they perform tasks which would take much time and trouble by ordinary chemical methods".[36] Use of microorganisms to produce chemicals and fuels like acetic acid and ethanol dates back to prehistoric times. One of the earliest commercial production of chemicals using microorganisms was in 1914 during the First World War. *Clostridium acetobutylicum* was used to convert starchy materials, such as corn, to acetone, butanol, and ethanol. Acetone was the raw material for the manufacture of cordite, used as a propellant for heavy artillery and small arms and ammunition.[37]

Manufacturing of these chemicals by biological means was made unattractive by the growth of petroleum based chemical industry. Chemists developed multi-step schemes to convert petroleum-derived hydrocarbons into bulk chemicals. Since the 1990s with the advent of Green Chemistry, microbes are poised to re-enter the production scene of bulk chemicals. Extensive progress in the last two decades on microbial genetics, various metabolic pathways, and the advent of molecular biology and genetic engineering has made it possible to turn microbes into one-pot chemical reactors in which multiple enzymatic steps can be performed.[38]

Metabolic pathways which are not normally present in a microorganism can now be introduced by cloning the required genes and expressing the enzymes. With these biotechnological advancements, there is a renewed emphasis on the use of carbohydrate feedstocks for the production of fuels and other chemicals. Examples being, use of genetically manipulated microbes to yields products of commercial importance like catechol and adipic acid from carbohydrates and anaerobic biodegradation of biomass for methane production.[39]

A specific example is the synthesis of an anticonvulsant drug LY300164 from Lilly laboratories, which is being developed for epilepsy and neurodegenerative disorders. Chemical synthesis generated a large volume of organic solvent and chromium. Significant environmental improvement was achieved by using a new synthetic strategy, which started with the biocatalytic reduction of a ketone to an optically pure alcohol using *Zygosaccharomyces rouxii*. Specific resin was used to adsorb the product leading to better product recovery. Using these modifications, 34000 L of solvent and 300 kg of chromium waste were eliminated for every 100 kg of LY 300164 produced.[40]

Advanced molecular biology techniques are being used to improve enzyme production, catalytic activities, and stability. This has resulted in the use of enzymes in diverse fields such as food technology, beverages, detergent manufacturing leather processing, etc. Following are a few specific examples. Lipases and Proteases are used in detergents for effective cleaning of clothes in cold water.[41] In textile industry biostoning of denim can now be carried out using enzymes instead of using acid or energy for agitation of pumice stones. Peroxidase is being used in place of toxic formaldehyde for the manufacture of phenolic resins. Leaching of acid bisulphite pulp using xylanases has been shown to significantly reduce the requirement of bioleaching chemicals.[42]

5.2 Photocatalysis:

When a proton is absorbed, it must transfer all its energy to the absorbing molecule, the molecule being promoted to a higher energy state. For many molecules, the energy required for promotion from the electric ground state to the lowest excited state falls in the visible and UV regions of the electromagnetic spectrum. For most molecules, the ground state is a singlet in which the two residing electron spins are paired. On absorption of the photon one electron is promoted to an unfilled orbital, the electron spin initially being retained to produce a singlet excited species. Although formally forbidden by selection rules, spin inversion to a lower energy triplet state, via a process called intersystem crossing, does frequently occur. The electronically excited molecule may then undergo a number of processes by which the excess energy is lost. Some of this does not result in a chemical reaction, reducing the quantum yield.[43-45]

A. Advantages and Challenges faced by Photochemical Processes.[46]

- Photons are very clean reagents, leaving no residues. A photoinitiated process, therefore has potential advantages even when compared to reactions initiated by the use of catalysts.
- Such processes may use fewer raw materials compared to photo- and radical-initiated halogenation reactions.
- Since the energy is more detected, reaction temperatures are generally low. This may give higher selectivities, by reducing by-product formation from competing reactions
- As will discussed more fully below, some reaction pathways are more readily available via photochemical processes, leading to products that would be difficult to make by other routes.

Although industry use has been limited:

- In photochemical processes even small amounts of fouling on the photochemical window or reactor wall through which the light has to pass can completely prevent a reaction from occurring. In thermal processes fouling can often be minimized through a selection of reactor materials, e.g., glass, stainless steel, Inconel, PTFE-lined, etc.; in photochemical processes, there is little flexibility in the choice of 'window' material owing to the requirement for transparency at a particular wavelength.[47]
- Radiation of a particular wavelength (monochromic) is required to initiate a specific electronic transition, but most UV and visible light sources are polychromatic. For

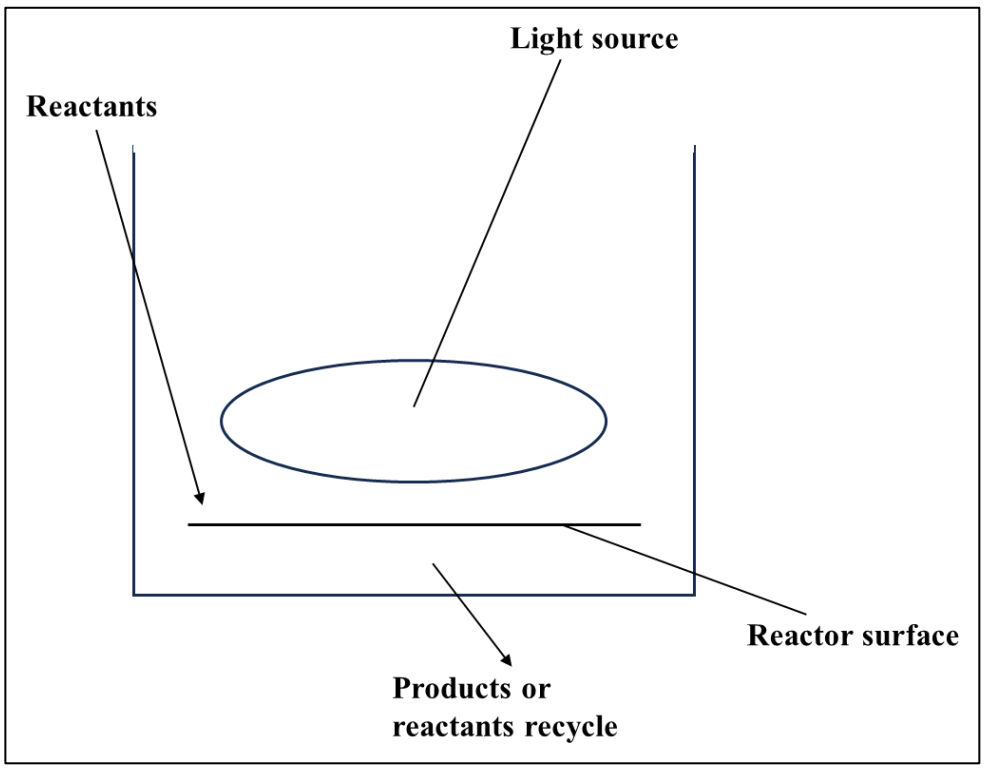
example, common mercury arc lamps emit around 50% of their energy in the 405 nm to 578 nm range. Hence, for most processes, well over half of the electrical energy supplied to the lamp is wasted, reducing the overall energy efficiency and increasing process costs. In addition, some lamps also emit some of their energy as heat, which again is wasteful of energy and necessitates the installation of a cooling device (frequently circulating cold water).[48]

- Light sources are often expensive, especially if made of thick-walled quartz as in high-pressure mercury lamps, and delicate, so equipment costs may be high compared to thermal processes.[49]
- Since the power of transmitted light drops off as the square of the distance from the light, for efficient reaction and energy usage the reactants must be as close as possible to the light source.[50]

In recent years significant research effort has gone into meeting these challenges with particular focus on the development of reactor technology.

B. Examples of Photochemical Reactions:

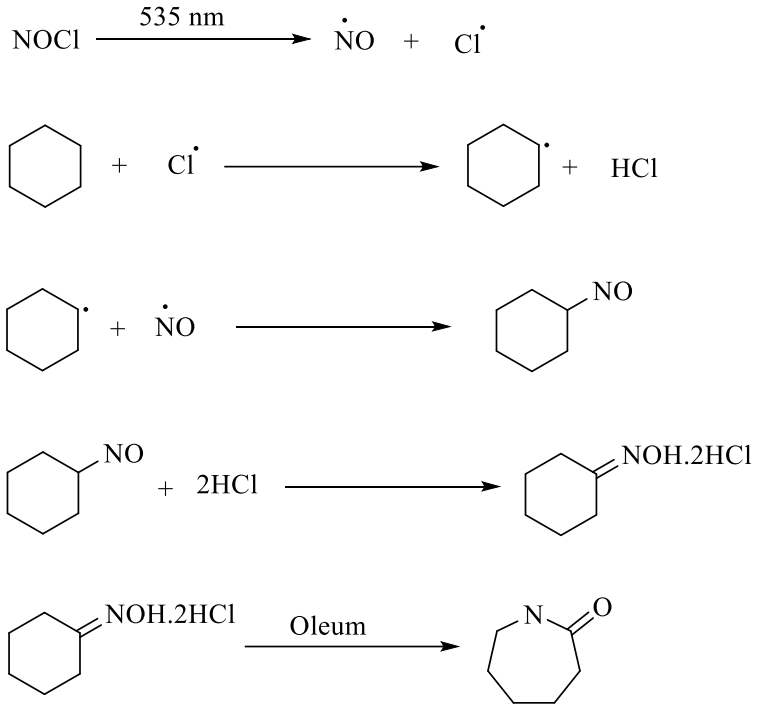
Synthesis of caprolactam and vitamin D3 is an excellent example of the scale at which such reactions can be successfully run, even though the quantum yield for this reaction is only 80%.[51]



Schematic illustration of 'non-contact' type photochemical reactor

The chemistry involves a radical process resulting from the production of NO and Cl radicals from NOCI by light of 535 nm wavelength. The commercial success of this process is partially due to the relatively low cost of producing this 'visible region' light, using a low-pressure mercury lamp doped with thallium iodide.

The thallium iodide both increases the intensity of the required wavelength and reduces the intensity of the lower wavelength, which initiates polymer formation; hence fouling is reduced to acceptable levels.[52] A continuous counter current flow reactor is used, the inside of which is made of glass. The reactants do not come into direct contact with the multi-lamp light source but pass through a thin adjacent glass vessel, which can be cleaned as required. The oxime salt passes out through the bottom of the reactor with unused gaseous reactants being recycled from the top of the reactor.[17]

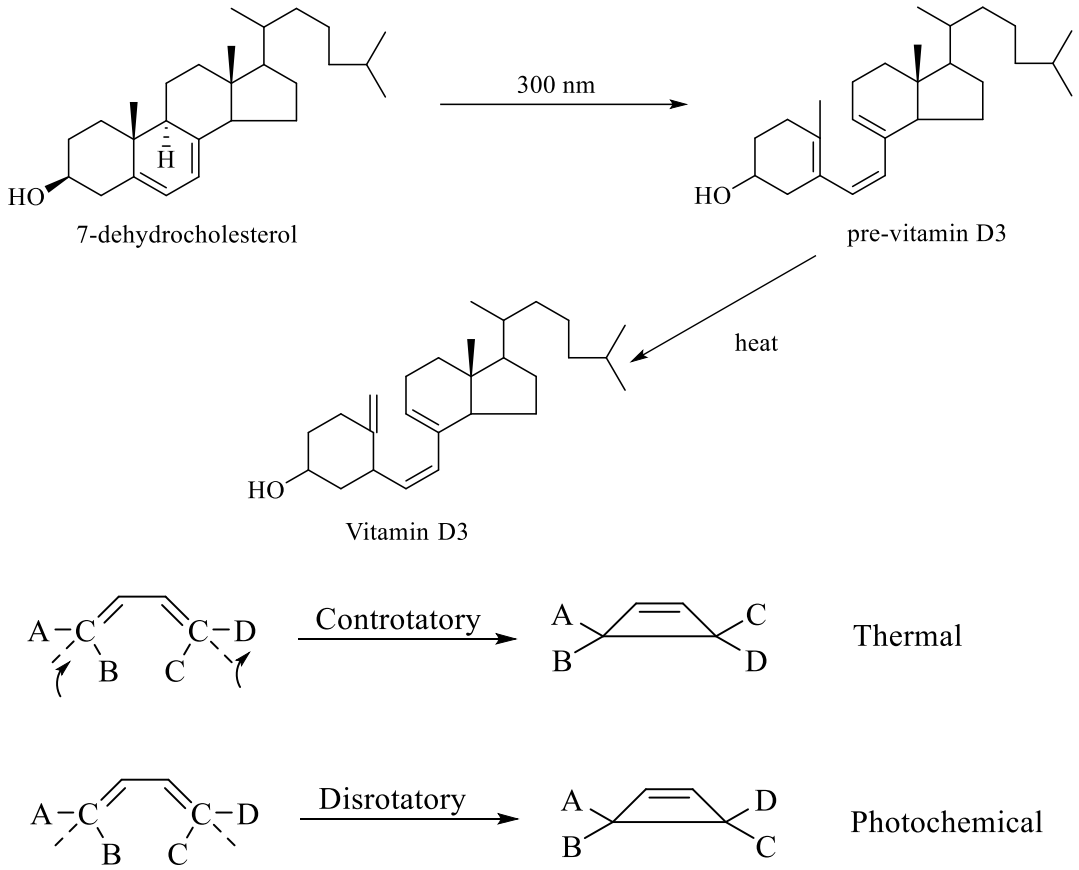


Photochemical caprolactam synthesis

Recent laboratory work has shown that cyclohexane can be oxidized in a high quantum yield reaction using photocatalysts based on iron porphyrins or tungstates.[53]

The other commonly quoted industrial photochemical process electrocyclic ring opening followed by a thermal 1,7-hydride shift (Scheme 1). This is a further example of a successful low-quantum yield process; in this case, there is no viable thermal alternative.[54]

Photochemistry offers the possibility of simple synthesis of some materials that would be very difficult to synthesize by other means. Stereoselective synthesis of four-membered rings is an excellent example of this (Scheme 2).[55]



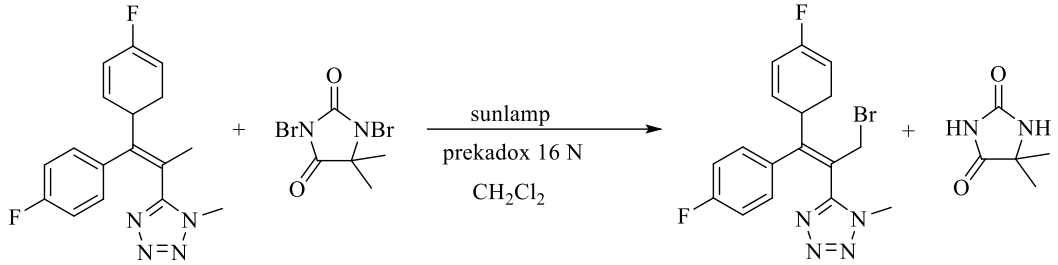
Scheme 2 Photochemical ring closure of diene

Photochemical free-radical reactions, exemplified by halogenation reactions. Chlorination of methane and synthesis of the degreasing solvent trichloroethane are commercial processes.

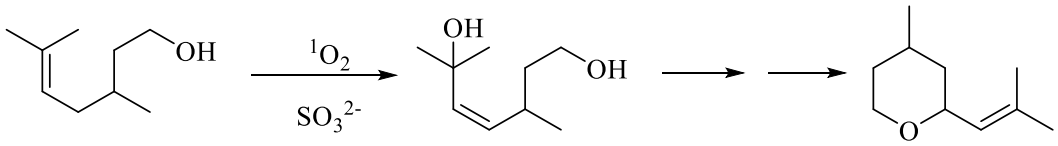
Whilst the process may have some green elements, the products of these reactions are being replaced by more environmentally friendly ones. An interesting free-radical bromination has been carried out at the 20kg scale (Scheme 3).[56] The unusual brominating agent N-bromosuccinamide, produced a very large exotherm. The pilot reactor simply consisted of a sunlamp around which the reactants flowed in a PTFE tube; again the process economics were helped by the fact that visible light could be used.[57]

Benzoquinone can be reacted with an aldehyde under a sunlamp to yield an acyl hydroquinone in up to 88% yield. The alternative procedure would involve the reaction of an acyl chloride with hydroquinone and a stoichiometric amount of aluminium chloride.

Oxidation reactions are also possible using singlet oxygen, generated using a sensitizer such as Rose Bengal. Potentially such a process could be used to replace once involving stoichiometric oxidants such as chromium oxide. Rose oxide has been made by a route involving singlet oxygen generation (Scheme 4).[58]



Scheme 3 Pilot scale example of a photochemical bromination



Scheme 4 Synthesis of rose oxide involving O_2

5.3 Photochemical Reactions:

The earliest known photochemical natural reaction is the photosynthesis of sugars by plants using sunlight, CO_2 and H_2O in the presence of chlorophyll.

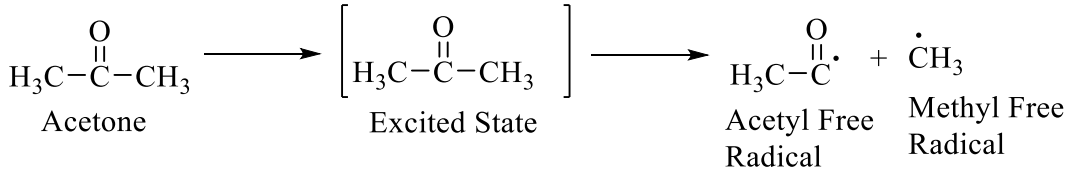
Photochemical Reactions of Some Carbonyl Compounds:

Carbonyl compounds, particularly ketones undergo very interesting photochemical reactions. Some of these are discussed below:

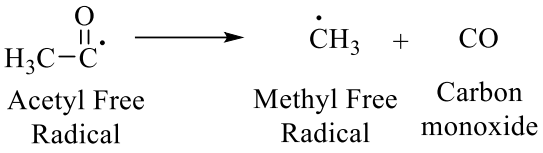
Photolysis of acetone (Propanone):

The term photolysis is used when light absorption of molecules leads to cleavage of bonds.

Absorption of light by acetone leads to the formation of an excited state, which has sufficient energy to undergo cleavage of a C-C bond (the weakest bond in the molecule) and forms a methyl free radical and an acetyl free radical.[59]

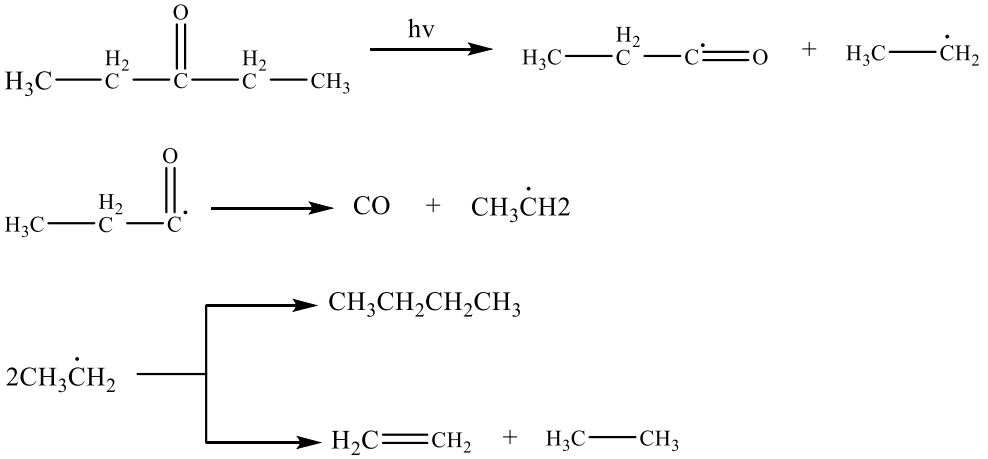


At a temperature much above room temperature, the acetyl radical breaks down to give another methyl radical and carbon monoxide.



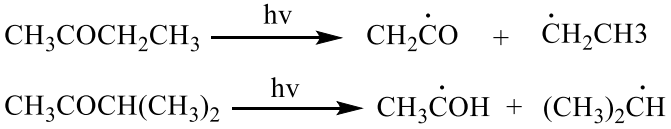
The products obtained on completion of the reaction are ethane and carbon monoxide.

In the case of photolysis of 3-pentanone $\left(CH_3CH_2-\overset{O}{\overset{\|}{C}}-\overset{H_2}{C}-CH_3\right)$ the $CH_3\dot{C}H_2$ radical forms, which can also undergo disproportionation in addition dimerization.

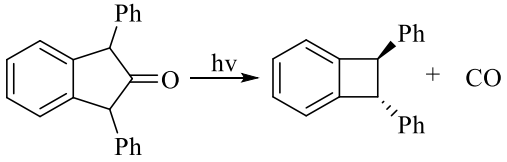


In the case of unsymmetrical ketones, splitting takes place in a way to generates the more stable of the two possible radicals.

5.4 Alternate Energy Processes in Chemical Synthesis:

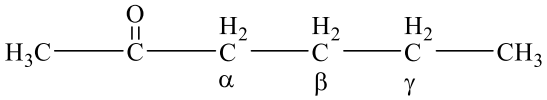


Photolytic decarbonylation of cyclic ketones produces cyclic hydrocarbons.

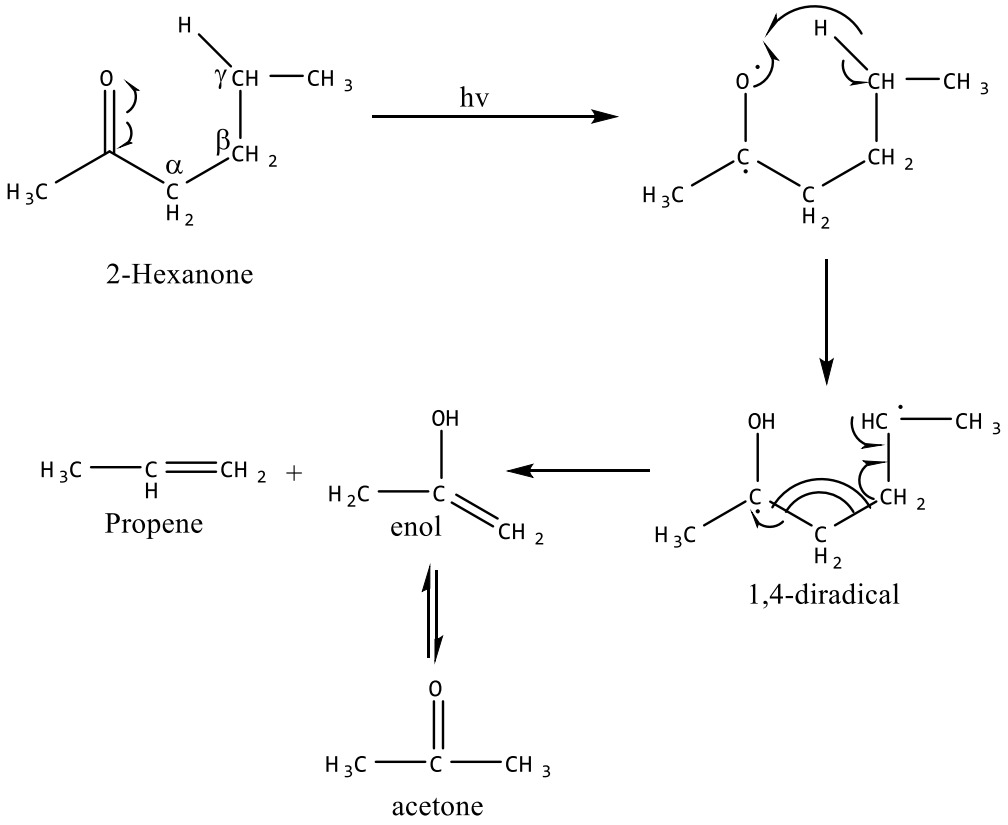


Photolysis to 2-hexanone:

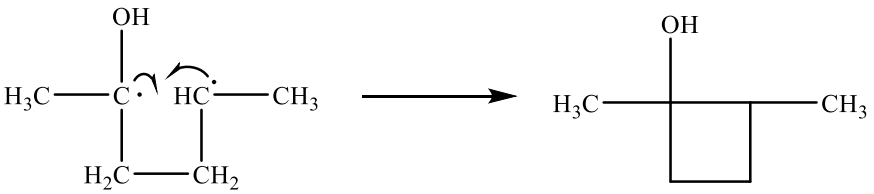
Ketone possessing a y-hydrogen atom (as in the case of a undergoes an interesting 2-



hexanone, photochemical reaction the course of which is different than that described above. In this case, the excited state of 2-hexanone undergoes an intramolecular hydrogen transfer (from y-carbon to the oxygen of the carbonyl group) with simultaneous fission of a-ß carbon-carbon bond in the alkyl group. The products of this reaction are an alkene and a simpler ketone (in its enolic form). This process is known as the Norrish type II reaction. This reaction proceeds by an initial y-hydrogen abstraction by the oxygen atom yielding a 1,4-biradical, which subsequently gives an olefin and an enol.[60]

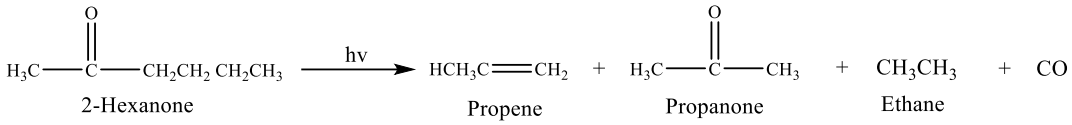


The 1,4-diradical can undergo ring closure to give a cyclobutene derivative.

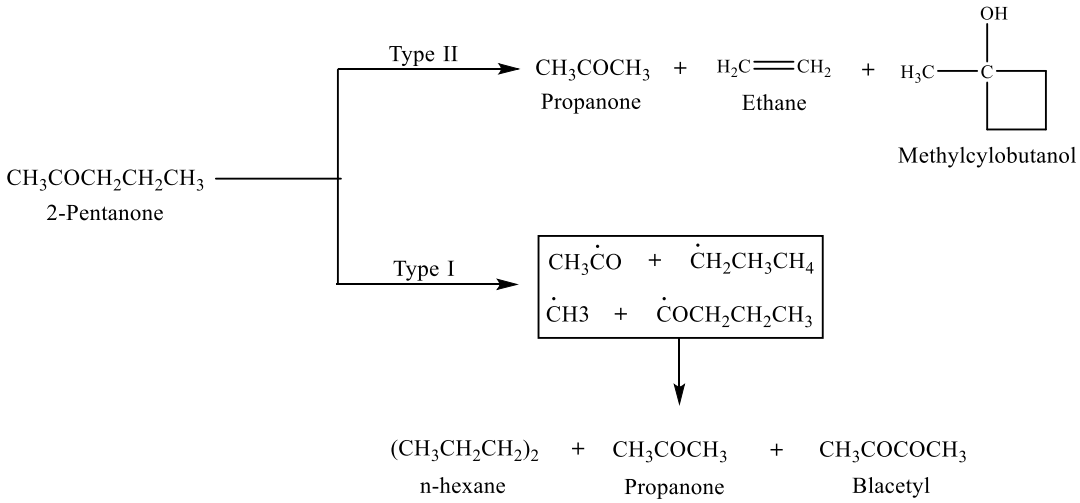


In the photolysis of 2-hexanone, Norrish type II cleavage is often accompanied by a Norrish type I process though to a lesser extent.

Propanone, the product of photolysis of 2-hexanone can undergo Norrish type I reaction and finally a complex mixture of products consisting of propene, propanone, ethane and carbon monoxide is formed.[61]

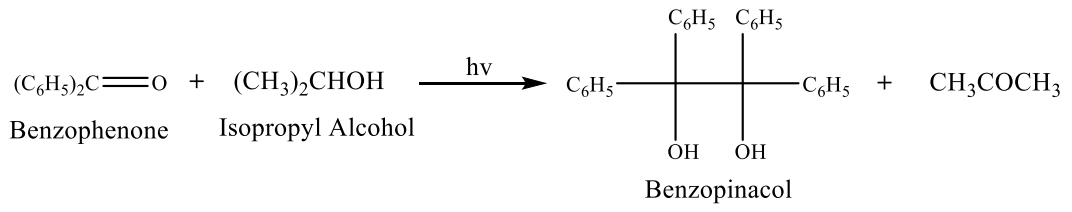


Similarly, irradiation of 2-pentanone yields the following products:



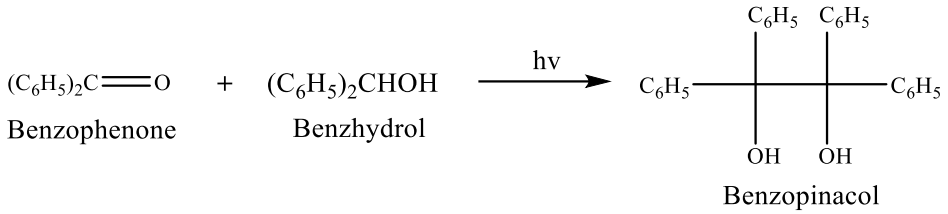
Photolysis of benzophenone:

Photolysis of benzophenone (in sunlight) in the presence of an alcoholic solvent (preferably isopropyl alcohol) gives benzo pinacol in quantum yield unity.[62]



It is well known that benzophenone by reduction with zine and acetic acid gives benzopinacol.

The photolysis reaction of benzophenone is known as photo reductive dimerization.



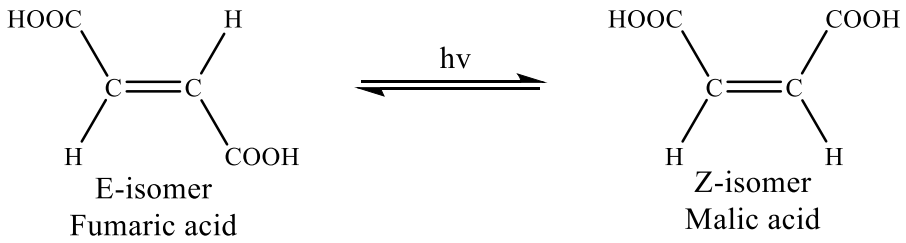
Photochemical Reactions of Olefins:

In the case of olefins, photochemical reactions involve two types of electronic absorption (i) α-π* excitation (requires more energy and is available only from light of wavelength lower than 150 nm so it is difficult to achieve under usual experimental conditions) and (ii) π→π* excitation (requires the absorption of light of about 180-210 nm for nonconjugated olefins and above 220 nm for conjugated olefins). Most of the photochemical reactions of olefins involve π→π* excitation.

The initial excitation generally occurs with no change in multiplicity and so a first singlet excited state is obtained.[63] Also, this transition (π→π*) is symmetry allowed. The singlet excited states of olefins have less tendency for intersystem crossing and are capable of initiating many photochemical reactions. However, the T, states of olefins are generated conveniently by intermolecular energy transfer from a triplet donor to an olefin molecule. The photochemistry of singlet excited state of an olefin differs from that of its triplet state.[64]

Isomerization of olefins:

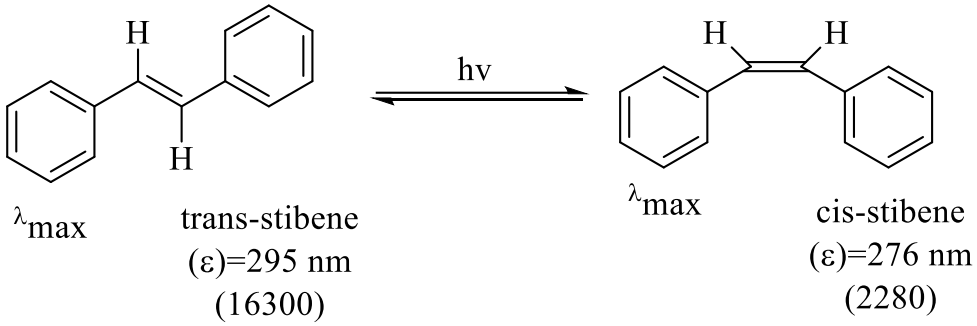
On irradiation with UV light, olefins undergo isomerization than the Z-isomer. Usually, an E-isomer is partially converted into its thermodynamically less stable Z-isomer. An example is the interconversion of fumaric and maleic acids.[65]



Photoisomerization of cis and trans-stilbene:

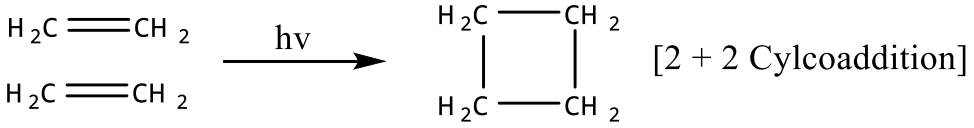
Olefines are known to exhibit geometrical isomerism. The photochemical cis-trans isomerization of stilbenes (1,2-diphenyl ethers) provides the simplest case of light-induced geometrical isomerisation. It is found that irradiation of trans-stilbene in hexane in UV light results in the formation of the cis-isomer.[66]

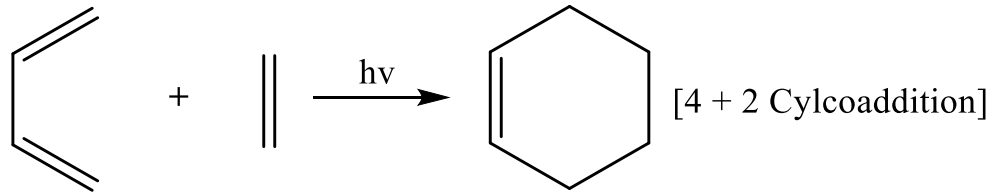
After some time the cis-trans ratio becomes constant and does not change if irradiation is continued. This condition is called a **photostationary state.**[67]



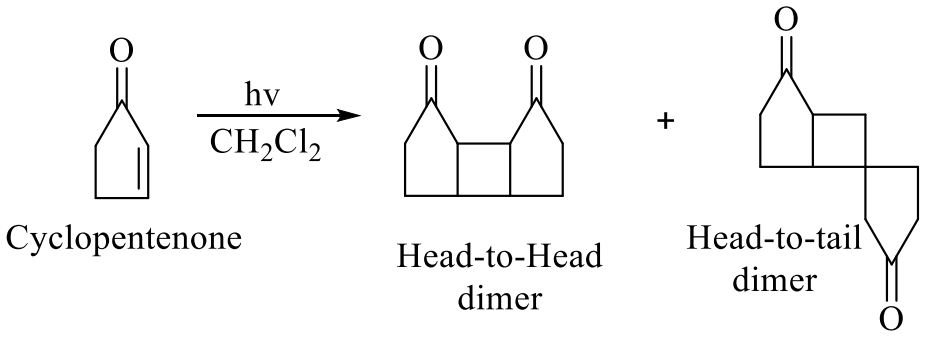
Photochemical Cycloaddition Reactions:

1,2- and 1, 4-cycloadditions occur photochemically with or without sensitizers. Examples of both 1,2- and 1,4-cycloadditions are given below:

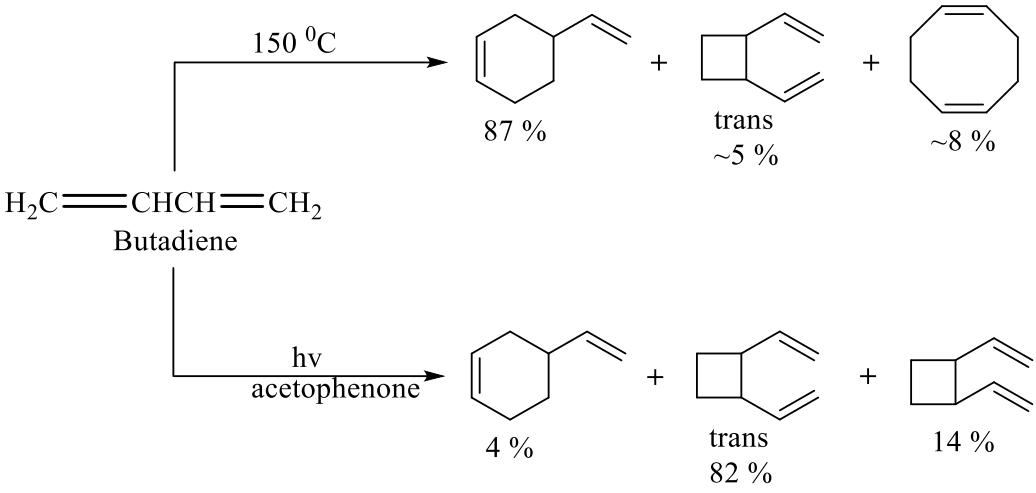




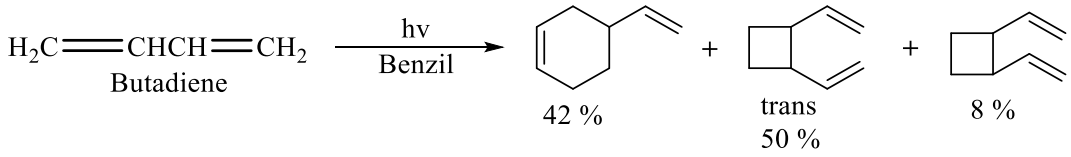
Photochemical cycloaddition of olefins gives a four-membered ring, which is a synthetically useful process. One familiar example is the dimerization of cyclopentenone on irradiation with light in dichloromethane to give a mixture of 'head-to-head' and 'head-to-tail' dimers. These dimers may be formed via an excimer (excited dimer) derived from the (π→л*) cyclopentenone and a molecule of ground-state cyclopentene.[68]



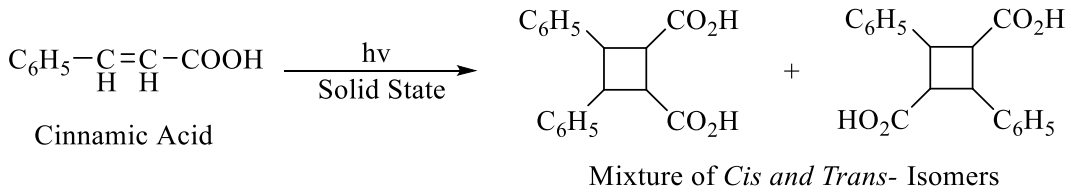
Butadiene provides an excellent example of the difference between thermal and photochemical cycloadditions.



It is found that the photochemical cycloaddition products of butadiene depend on the sensitizer used.

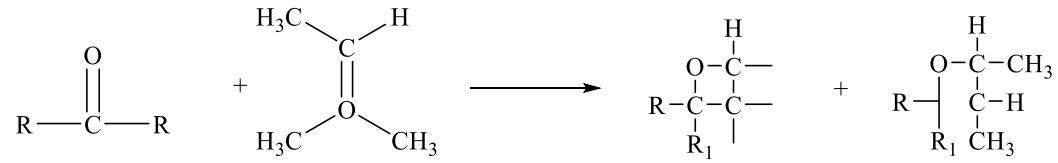


Following are given examples of many photochemical dimerization reactions.

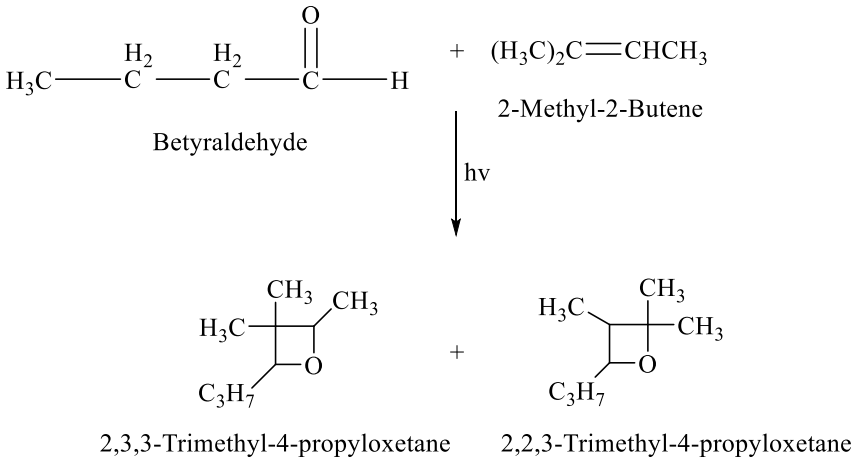


Mixture of *Cis and Trans*- Isomers

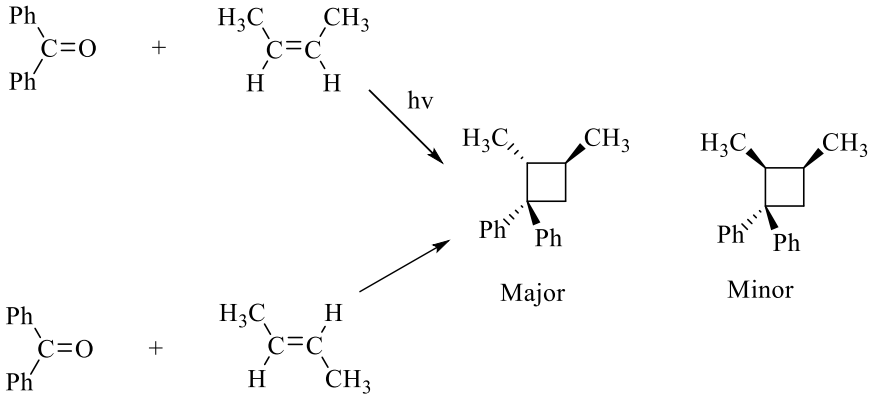
A very interesting photochemical cycloaddition reaction is the addition of carbonyl compounds to olefins to yield oxetanes (oxa-cyclobutanes).



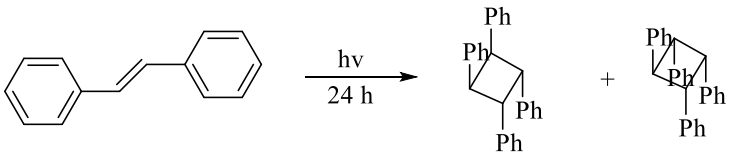
This reaction is known as the **Paterno-Buchi reaction**. For example, photocycloaddition of butyraldehyde to 2-methyl-2-butene yields a mixture of 2,3,3-trimethyl-4-propyloxetane and 2, 2, 3-trimethyl-4-propyloxetane.[69]



The Paterno-Buchi reaction normally occurs by the cycloaddition of the triplet state of the carbonyl compound with the ground state of an alkene. The photocycloaddition of benzophenone with cis- and trans-2- butene gives the same mixture of cis- and trans-oxetanes. This shows that the reaction is not stereospecific. The lack of stereochemical discrimination clearly shows that the reaction is not concerted and the ring is formed in two stages.[70]



Stribenes, photodimerize efficiently in water. The same reaction in solvents like benzene leads mainly to cis-trans isomerisations. The yield of dimerisation is increased by the addition of LiCl (increasing hydrophobic effect. However, the yield decreased with addition of guanidium chloride (decreasing the hydrophobic effect)[71]

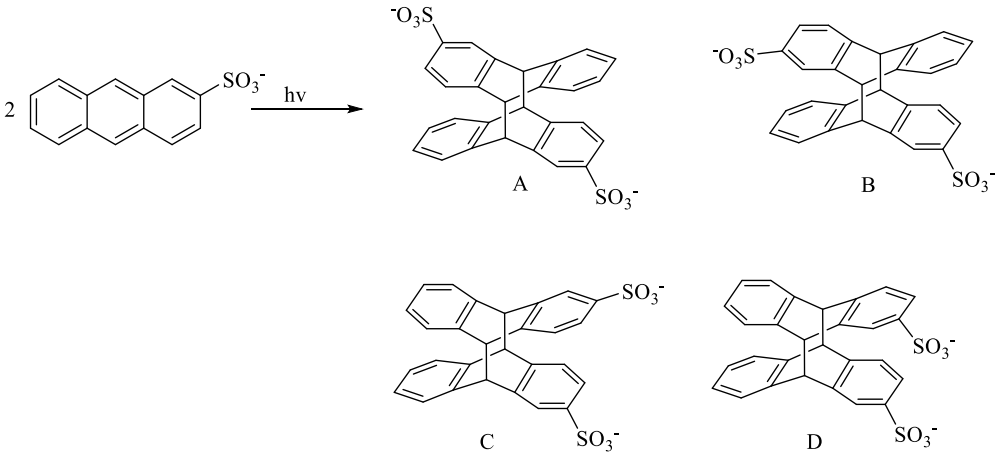


Benzene
Water
Water + LiCl
Water + gunidinium chloride

Photochemical Reactions in Micellar Media:

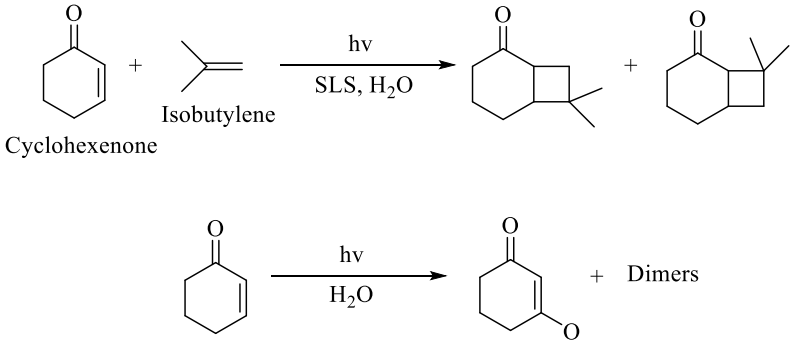
In case a surfactant is added to water, it will aggregate in the formation of micelles. It has been found that the formation of such micelles has a significant effect on the regio- and stereoselectivity of photochemical reactions.[72] In such a micellar case, the hydrophobic interior of micelles provides a hydrophobic pocket within the bulk water solvent. A similar situation of hydrophobic pocket is to use cyclodextrin. Thus, selectivity in product formation can also be expected in this case. Following are some of the photochemical reactions in micellar media:[73]

Photodimerization of anthracene-2-sulfonate: The photo dimerisation of anthracene-2-sulfonate in micellar media (water containing a surfactant) gives four products (A-D). However, if the same reaction is carried out in the presence of ß- cyclodextrin. Only the isomer A is obtained.

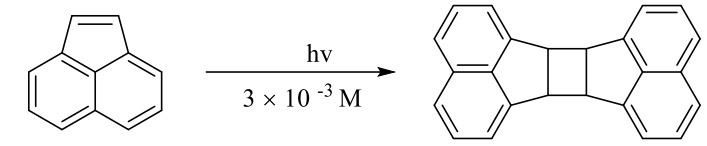


Medium	Product (A:B:C:D)
Water	1: 0.8: 0.4: 0.05
Water + β-CD	A only

Cycloaddition of isobutylene to cyclohexenone in micellar media gave a mixture of bicycloproducts. However, inhomogeneous aqueous phase, cyclohexenone gives the expected y-keto alcohol.[74]



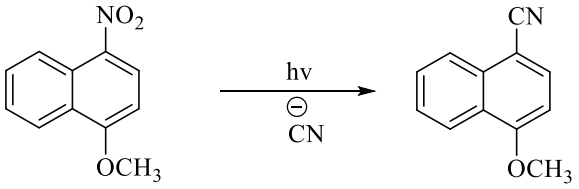
Photodimerization of acenaphthylene in micelle-containing solutions gives the dimeric product. Such products are not obtained in benzene.



Acenaphthylene

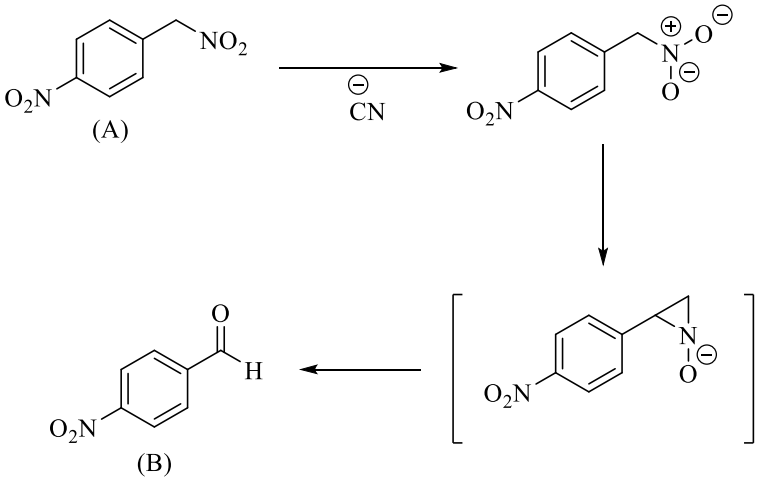
SLS	96%
C_6H_6	0%

Photoinduced substitution of aromatic compounds: Photoexcitation of aqueous solution of 4-methoxy-1-nitronaphthalene (A) containing CN ions results in the formation of 4-methoxy-1-naphthalene carbonitrile (B).[75]



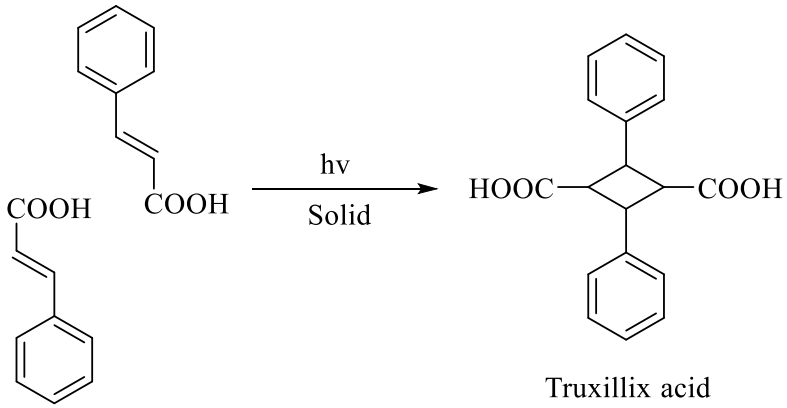
(A) (B)

The photorearrangement of 4-nitrophenyl-nitromethane (A) into 4-nitrobenzaldehyde (B) was found to be much more efficient in a cationic detergent (CTAC) than in a basic ethanol-water solution.[74]



Photochemical Reactions in Solid State There are few reports of photochemical reactions in the solid state:

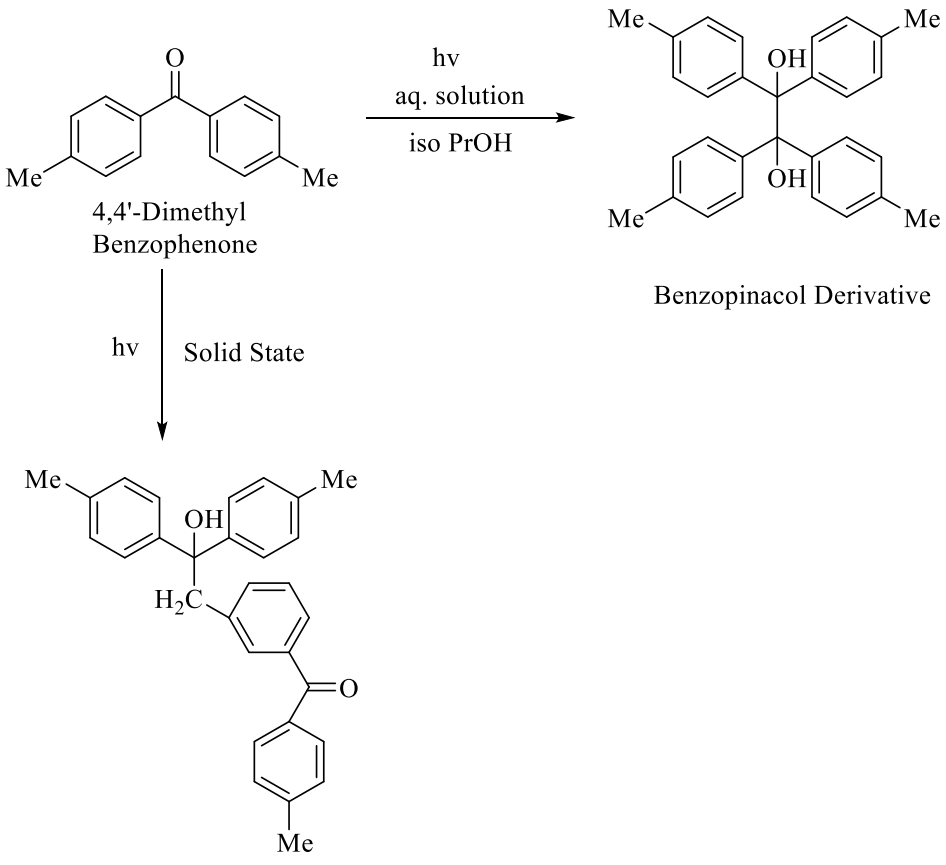
Cinnamic acid (single crystal) on photoirradiation gives truxillic acid.



Cinnamic Acid
(single cyrstal)

Truxillix acid
(single cyrstal)

Photoirradiation of 4,4'-dimethyl benzophenone in a solid state gave a dimeric product. It is, of course, well known that photoirradiation of 4,4'-dimethyl benzophenone in isopropyl alcohol gives benzopinacol derivative in quantitative yield.[76]



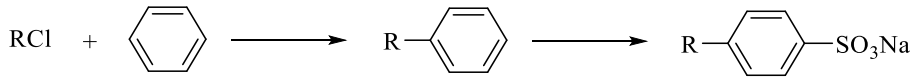
4,4'-Dimethyl
Benzophenone

Benzopinacol Derivative

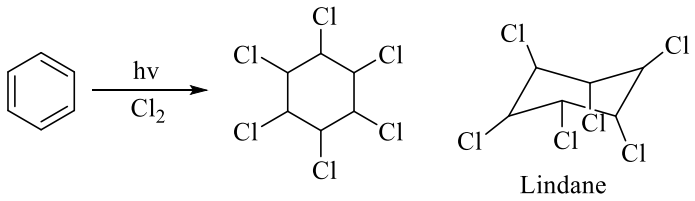
Dimeric Product

Free Radical Chlorination

The chloroalkanes find a use for the alkylation of benzene to give alkylbenzenes, which are starting materials for alkylbenzene sulfonates, an important class of detergents.

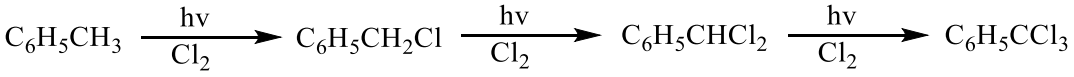


Photochemical chlorination of benzene to produce hexachlorocyclohexane.



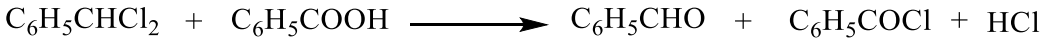
The photoaddition of chlorine to benzene serves for the production of the y-isomer of hexachlorocyclohexane, a versatile insecticide marketed as Lindane or Gammexane (y-BHC). The yield of 15%, however, is very modest.[77]

The photochlorination of toluene to benzyl chloride, benzylidene dichloride and benzotrichloride, is a very well-known procedure.



Mixtures of the first two, viz. benzyl chloride and benzylidene dichloride are produced in specially designed photoreactors at 80-110°C.

Benzyl chloride is also obtained by purely thermal chlorination of toluene and is mainly converted into benzyl alcohol, a well-known fragrance. It is also used in the synthesis of drugs, disinfectants, and emulsifiers. On hydrolysis or preferably on reaction with benzoic acid, benzylidene dichloride yields benzaldehyde; in the latter case a valuable intermediate, benzoyl chloride is also obtained.[77]



Free Radical Sulfochlorination:

Photochemical sulfochlorination of paraffins is of great industrial importance. In sulfochlorination, the function of light is for the formation of chlorine atoms from chlorine. The sulfonyl chloride group is distributed almost randomly over all the C atoms of the hydrocarbon chain.[78]

$$RH + SO_2 + Cl_2 \xrightarrow{hv} RSO_3Cl + HCl$$

RH = Mixture of n-alkanes

Industrial sulfochlorination has been reviewed by Lindner. The alkyl sulfonyl chlorides, thus produced are hydrolysed by caustic soda to give water-soluble alkanesulfonates, which are mainly used as emulsifiers for polymerisation.[77]

$$RSO_3Cl + 2\,NaOH \longrightarrow RSO_3Na + NaCl + H_2O$$

The reaction of alkane sulfonyl chlorides with ammonia gives sulfonamides, which are used as textile auxiliaries. The sulfonamides further react with chloroacetic acid to give a mixture of sulfonylaminoacetic acids. These types of compounds serve as emulsifiers and as anticorrosion agents for mineral oils.[79]

$$RSO_3Cl \xrightarrow[NH_3]{} RSO_3NH_2 \xrightarrow[NaOH]{ClCH_2CO_2H} RSO_2NHCH_2CO_2H$$

Photochemical Sulfoxidation:

A convenient synthesis of alkanesulfonates is by the sulfoxidation process. In this procedure, oxygen serves as an oxidizing agent instead of chlorine used earlier.

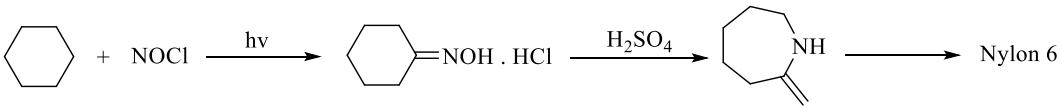
$$RH + SO_2 + 1/2\,O_2 \longrightarrow RSO_3H$$

$$RSO_3H + NaOH \longrightarrow RSO_3Na + H_2O$$

$RH = C_{14\text{-}18}$ -n-alkane

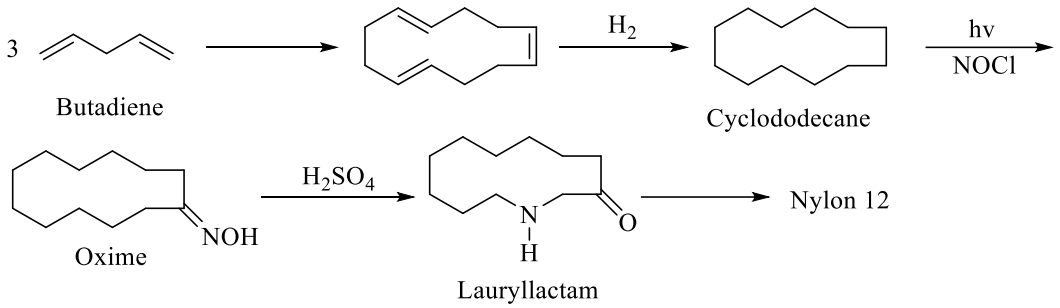
Photonitrosation:

The light-induced reaction of nitrosyl chloride with cyclohexane gives cyclohexane oxime, which is a starting material for the synthesis of caprolactam, the monomer of nylon 6.



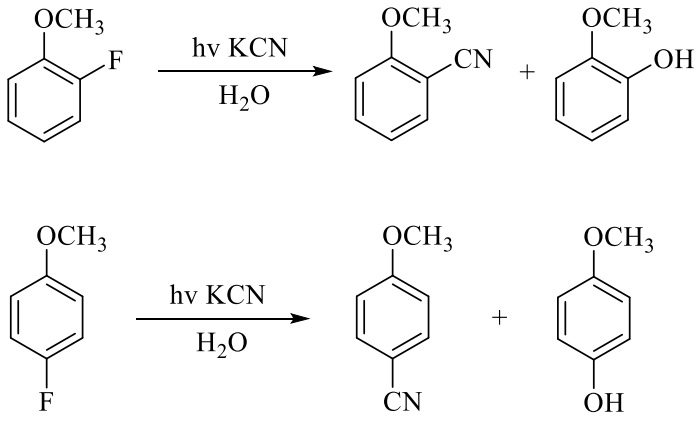
Another industrial application of photonitrosation is the manufacture of lauryl lactam, which is a starting material for the production of Nylon 12. In this procedure, cyclododecane, [which is obtained from butadiene in two steps] is converted into oxime by nitrosyl chloride in high yield. The oxime in reaction with acid gives lauryl lactam, the monomer of nylon-12.[80]

Lauryllactam, due to its low density and low absorption of water, is used for a number of special purposes like production of dimensionally stable plastic components (automobile construction) and for the plastic coating of metals.[81]



Photochemical Aromatic Substitution:

Irradiation of o-fluoro anisole in the presence of aqueous potassium cyanide solution gives catechol monomethyl ether as the major product. However, irradiation of p-fluoro anisole in the presence of aqueous potassium cyanide solution gives p-cyano anisole as the major product.



5.5 References:

1. Van Durme, J.; Dewulf, J.; Leys, C.; Van Langenhove, H. Combining non-thermal plasma with heterogeneous catalysis in waste gas treatment: A review. *Applied Catalysis B: Environmental* **2008**, *78* (3-4), 324-333.
2. Mustafa, M. G.; Khan, M. G. M.; Nguyen, D.; Iqbal, S. Techniques in biotechnology: Essential for industry. In *Omics technologies and bio-engineering*, Elsevier, 2018; pp 233-249.
3. Burg, J. M.; Cooper, C. B.; Ye, Z.; Reed, B. R.; Moreb, E. A.; Lynch, M. D. Large-scale bioprocess competitiveness: the potential of dynamic metabolic control in two-stage fermentations. *Current Opinion in Chemical Engineering* **2016**, *14*, 121-136.
4. Korpics, K. Metabolic Engineering VII Conference. 2012; Engineering Conferences International Inc.

5. Keller, M. A.; Piedrafita, G.; Ralser, M. The widespread role of non-enzymatic reactions in cellular metabolism. *Current opinion in biotechnology* **2015**, *34*, 153-161.
6. Held, M.; Schmid, A.; Van Beilen, J.; Witholt, B. Biocatalysis. Biological systems for the production of chemicals. *Pure and Applied Chemistry* **2000**, *72* (7), 1337-1343.
7. Reetz, M. T. Biocatalysis in organic chemistry and biotechnology: past, present, and future. *Journal of the American Chemical Society* **2013**, *135* (34), 12480-12496.
8. Pei-Ran, C.; Jian-Xin, G.; Zbi-Liang, W.; Shi-Qing, H.; Zn-Yi, L.; Guo-Qiang, L. Asymmetric syntheses aided by biocatalysts. *Chinese Journal of Chemistry* **2003**, *21* (8), 983-993.
9. Kamerbeek, N. M.; Fraaije, M. W.; Janssen, D. B. Identifying determinants of NADPH specificity in Baeyer–Villiger monooxygenases. *European journal of biochemistry* **2004**, *271* (11), 2107-2116.
10. Schrittwieser, J. H.; Velikogne, S.; Hall, M. l.; Kroutil, W. Artificial biocatalytic linear cascades for preparation of organic molecules. *Chemical reviews* **2018**, *118* (1), 270-348.
11. Blamey, J. M.; Fischer, F.; Meyer, H.-P.; Sarmiento, F.; Zinn, M. Enzymatic biocatalysis in chemical transformations: a promising and emerging field in green chemistry practice. In *Biotechnology of microbial enzymes*, Elsevier, 2017; pp 347-403.
12. Mubofu, E. B. SUPPORTED CATALYSTS AND REAGENTS FOR GREEN CHEMISTRY. *Green Chemistry: Environment Friendly Alternatives* **2003**, 149.
13. Boodhoo, K.; Flickinger, M.; Woodley, J.; Emanuelsson, E. Bioprocess intensification: A route to efficient and sustainable biocatalytic transformations for the future. *Chemical Engineering and Processing-Process Intensification* **2022**, *172*, 108793.
14. Gao, F. A Study of Polymer-Small Molecule Interactions for Solid-Liquid Two Phase Partitioning Bioreactors With Emphasis on the Bioproduction of 2-Phenylethanol. Citeseer, 2009.
15. Slagman, S.; Fessner, W.-D. Biocatalytic routes to anti-viral agents and their synthetic intermediates. *Chemical Society Reviews* **2021**, *50* (3), 1968-2009.
16. Abdelraheem, E. M.; Busch, H.; Hanefeld, U.; Tonin, F. Biocatalysis explained: from pharmaceutical to bulk chemical production. *Reaction Chemistry & Engineering* **2019**, *4* (11), 1878-1894.
17. Brahmachari, G.; Demain, A. L.; Adrio, J. L. *Biotechnology of microbial enzymes: production, biocatalysis and Industrial applications*; Academic Press, 2016.
18. Sheldon, R. A.; Woodley, J. M. Role of biocatalysis in sustainable chemistry. *Chemical reviews* **2018**, *118* (2), 801-838.
19. Rios, J.; Lebeau, J.; Yang, T.; Li, S.; Lynch, M. D. A critical review on the progress and challenges to a more sustainable, cost competitive synthesis of adipic acid. *Green Chemistry* **2021**, *23* (9), 3172-3190.
20. Vardon, D. R.; Rorrer, N. A.; Salvachúa, D.; Settle, A. E.; Johnson, C. W.; Menart, M. J.; Cleveland, N. S.; Ciesielski, P. N.; Steirer, K. X.; Dorgan, J. R. cis, cis-Muconic acid: separation and catalysis to bio-adipic acid for nylon-6, 6 polymerization. *Green Chemistry* **2016**, *18* (11), 3397-3413.
21. Kruyer, N. S.; Peralta-Yahya, P. Metabolic engineering strategies to bio-adipic acid production. *Current opinion in biotechnology* **2017**, *45*, 136-143.
22. Han, L.; Liu, P.; Sun, J.; Wu, Y.; Zhang, Y.; Chen, W.; Lin, J.; Wang, Q.; Ma, Y. Engineering catechol 1, 2-dioxygenase by design for improving the performance of the cis, cis-muconic acid synthetic pathway in Escherichia coli. *Scientific reports* **2015**, *5* (1), 13435.

23. Yang, W.; Xu, H. Industrial fermentation of vitamin C. *Industrial biotechnology of vitamins, biopigments, and antioxidants* **2016**, 161-192.
24. Vandamme, E. J. Production of vitamins, coenzymes and related biochemicals by biotechnological processes. *Journal of Chemical Technology & Biotechnology* **1992**, *53* (4), 313-327.
25. Ping, Y.; Wang, L.; Ding, Q.; Peng, Y. Nitrile as a versatile directing group for C (sp2)–H functionalizations. *Advanced Synthesis & Catalysis* **2017**, *359* (19), 3274-3291.
26. Survase, S. A.; Bajaj, I. B.; Singhal, R. S. Biotechnological production of vitamins. *Food Technology & Biotechnology* **2006**, *44* (3).
27. Vulsteke, E.; Van Den Hende, S.; Bourez, L.; Capoen, H.; Rousseau, D. P.; Albrecht, J. Economic feasibility of microalgal bacterial floc production for wastewater treatment and biomass valorization: A detailed up-to-date analysis of up-scaled pilot results. *Bioresource technology* **2017**, *224*, 118-129.
28. Yadav, P.; Chauhan, A. K.; Singh, R. B.; Khan, S.; Halabi, G. Organic acids: microbial sources, production, and applications. In *Functional foods and nutraceuticals in metabolic and non-communicable diseases*, Elsevier, 2022; pp 325-337.
29. D'Este, M.; Alvarado-Morales, M.; Angelidaki, I. Amino acids production focusing on fermentation technologies–A review. *Biotechnology advances* **2018**, *36* (1), 14-25.
30. Hoff, B.; Plassmeier, J.; Blankschien, M.; Letzel, A. C.; Kourtz, L.; Schröder, H.; Koch, W.; Zelder, O. Unlocking Nature's Biosynthetic Power—Metabolic Engineering for the Fermentative Production of Chemicals. *Angewandte Chemie International Edition* **2021**, *60* (5), 2258-2278.
31. Ran, N.; Zhao, L.; Chen, Z.; Tao, J. Recent applications of biocatalysis in developing green chemistry for chemical synthesis at the industrial scale. *Green Chemistry* **2008**, *10* (4), 361-372.
32. Hemashenpagam, N.; Selvajeyanthi, S. Removal of Phenolic Compound from Wastewater Using Microbial Fuel Cells. In *Microbial Fuel Cells for Environmental Remediation*, Springer, 2022; pp 279-297.
33. Ramachandran, P. A.; Shonnard, D.; Hesketh, R.; Fichana, D.; Stewart Slater, C.; Lindner, A.; Nguyen, N.; Engler, R. Green engineering: integration of green chemistry, pollution prevention, risk-based considerations, and life cycle analysis. *Handbook of Industrial Chemistry and Biotechnology* **2017**, 1921-1994.
34. Balderas-Hernández, V. E.; Treviño-Quintanilla, L. G.; Hernández-Chávez, G.; Martinez, A.; Bolívar, F.; Gosset, G. Catechol biosynthesis from glucose in Escherichia coli anthranilate-overproducer strains by heterologous expression of anthranilate 1, 2-dioxygenase from Pseudomonas aeruginosa PAO1. *Microbial cell factories* **2014**, *13*, 1-11.
35. Wu, S.; Chen, W.; Lu, S.; Zhang, H.; Yin, L. Metabolic engineering of shikimic acid biosynthesis pathway for the production of shikimic acid and its branched products in microorganisms: advances and prospects. *Molecules* **2022**, *27* (15), 4779.
36. Rocha, J. F.; Pina, A. F.; Sousa, S. F.; Cerqueira, N. M. PLP-dependent enzymes as important biocatalysts for the pharmaceutical, chemical and food industries: a structural and mechanistic perspective. *Catalysis Science & Technology* **2019**, *9* (18), 4864-4876.
37. Demain, A. L.; Vandamme, E. J.; Collins, J.; Buchholz, K. History of industrial biotechnology. *Industrial biotechnology: microorganisms* **2017**, *1*, 1-84.
38. Menon, V.; Rao, M. Trends in bioconversion of lignocellulose: biofuels, platform chemicals & biorefinery concept. *Progress in energy and combustion science* **2012**, *38* (4), 522-550.

39. Cheng, H.-H.; Whang, L.-M. Resource recovery from lignocellulosic wastes via biological technologies: Advancements and prospects. *Bioresource technology* **2022**, *343*, 126097.
40. Anderson, B. A.; Hansen, M. M.; Vicenzi, J. T.; Zmijewski, M. J. Chemistry, Biocatalysis and Engineering: An Interdisciplinary Approach to the Manufacture of the Benzodiazepine Drug Candidate LY300164. In *Process Chemistry in the Pharmaceutical Industry*, CRC Press, 1999; pp 289-308.
41. Sarmah, N.; Revathi, D.; Sheelu, G.; Yamuna Rani, K.; Sridhar, S.; Mehtab, V.; Sumana, C. Recent advances on sources and industrial applications of lipases. *Biotechnology progress* **2018**, *34* (1), 5-28.
42. Chandra, P.; Enespa; Singh, R.; Arora, P. K. Microbial lipases and their industrial applications: a comprehensive review. *Microbial cell factories* **2020**, *19*, 1-42.
43. Steiner, U. E. Fundamentals of Photophysics, Photochemistry, and Photobiology. In *Photodynamic Therapy: From Theory to Application*, Springer, 2014; pp 25-58.
44. Douglas, P.; Burrows, H. D.; Evans, R. C. Foundations of photochemistry: a background on the interaction between light and molecules. In *Applied photochemistry*, Springer, 2013; pp 1-88.
45. Zhao, J.; Ji, S.; Chen, Y.; Guo, H.; Yang, P. Excited state intramolecular proton transfer (ESIPT): from principal photophysics to the development of new chromophores and applications in fluorescent molecular probes and luminescent materials. *Physical Chemistry Chemical Physics* **2012**, *14* (25), 8803-8817.
46. Granone, L.; Sieland, F.; Zheng, N.; Dillert, R.; Bahnemann, D. Photocatalytic conversion of biomass into valuable products: a meaningful approach? *Green chemistry* **2018**, *20* (6), 1169-1192.
47. Darwish, S.; Ahmed, N.; Alahmari, A. M. Laser Beam Machining, Laser Beam Hybrid Machining, and Micro-channels Applications and Fabrication Techniques. *Machining, Joining and Modifications of Advanced Materials* **2016**, 171-269.
48. Shen, C.; Shang, M.; Zhang, H.; Su, Y. A UV-LEDs based photomicroreactor for mechanistic insights and kinetic studies in the norbornadiene photoisomerization. *AIChE Journal* **2020**, *66* (2), e16841.
49. Boger, J.; Hahn, R.; Rowley, J.; Carter, A.; Hollebone, B.; Kessler, D.; Blevis, I.; Dalnoki-Veress, F.; DeKok, A.; Farine, J. The Sudbury neutrino observatory. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* **2000**, *449* (1-2), 172-207.
50. Khan, A. A.; Tahir, M. Recent advancements in engineering approach towards design of photo-reactors for selective photocatalytic CO2 reduction to renewable fuels. *Journal of CO2 Utilization* **2019**, *29*, 205-239.
51. Noël, T.; Escriba Gelonch, M.; Huvaere, K. Industrial photochemistry: from laboratory scale to industrial scale. *Photochemical Processes in Continuous-Flow Reactors* **2017**, 245-267.
52. Dohi, T.; Yamaoka, N.; Kita, Y. Fluoroalcohols: versatile solvents in hypervalent iodine chemistry and syntheses of diaryliodonium (III) salts. *Tetrahedron* **2010**, *66* (31), 5775-5785.
53. Xiao, Y.; Liu, J.; Mai, J.; Pan, C.; Cai, X.; Fang, Y. High-performance silver nanoparticles coupled with monolayer hydrated tungsten oxide nanosheets: The structural effects in photocatalytic oxidation of cyclohexane. *Journal of colloid and interface science* **2018**, *516*, 172-181.

54. Burdett, K. A. *The synthesis and photochemistry of substituted 3, 4-and 1, 2-benzotropilidenes, benzonorcaradienes, and homo-benzotropilidenes*; The Ohio State University, 1974.
55. Hoffmann, N. Photochemical reactions as key steps in organic synthesis. *Chemical Reviews* **2008**, *108* (3), 1052-1103.
56. Juliá, F.; Constantin, T.; Leonori, D. Applications of halogen-atom transfer (XAT) for the generation of carbon radicals in synthetic photochemistry and photocatalysis. *Chemical Reviews* **2021**, *122* (2), 2292-2352.
57. Yang, Y.; Pignatello, J. J. Participation of the halogens in photochemical reactions in natural and treated waters. *Molecules* **2017**, *22* (10), 1684.
58. Wan, L.; Jiang, M.; Cheng, D.; Liu, M.; Chen, F. Continuous flow technology-a tool for safer oxidation chemistry. *Reaction Chemistry & Engineering* **2022**, *7* (3), 490-550.
59. Haas, Y. Photochemical α-cleavage of ketones: revisiting acetone. *Photochemical & Photobiological Sciences* **2004**, *3*, 6-16.
60. Formosinho, S. J.; Arnaut, L. G. A unified view of ketone photochemistry. *Advances in photochemistry* **1991**, *16*, 67-117.
61. Cicchetti, O. Mechanisms of oxidative photodegradation and of UV stabilization of polyolefins. In *Fortschritte der Hochpolymeren-Forschung*, Springer, 2006; pp 70-112.
62. Zhang, Z. *Photochemical Study of Vitamin K and Vitamin B Derivatives and Their Applications as Photo-induced Antimicrobial Agents*; University of California, Davis, 2021.
63. Carach, C. A. *Understanding Polymer-Fullerene Morphology in Organic Solar Cells via Photoluminescence, Raman Scattering, and Spectroscopic Imaging*; University of California, Santa Barbara, 2014.
64. Dinda, B.; Dinda, B. Principles of Photochemical Reactions. *Essentials of Pericyclic and Photochemical Reactions* **2017**, 181-214.
65. Ahluwalia, V.; Ahluwalia, V. Stereochemistry of Organic Alicyclic Compounds Containing Carbon–Carbon Double Bonds (Alkenes and Cycloalkenes). *Stereochemistry of Organic Compounds* **2022**, 39-71.
66. Cundall, R. Photophysical Processes in Condensed Phases. *Photochemistry: Volume 18* **2007**, 3.
67. Görner, H.; Kuhn, H. J. Cis-trans photoisomerization of stilbenes and stilbene-like molecules. *Advances in photochemistry* **1994**, *19*, 1-117.
68. Kaur, N.; Devi, M.; Verma, Y.; Grewal, P.; Bhardwaj, P.; Ahlawat, N.; Jangid, N. K. Photochemical Synthesis of Fused Five-membered O-heterocycles. *Current Green Chemistry* **2019**, *6* (3), 155-183.
69. Arora, G.; Rana, P.; Sharma, R. K. Greening Energy Sources. In *Green Chemistry for Beginners*, Jenny Stanford Publishing, 2021; pp 161-203.
70. Porco, J.; Schreiber, S. L. The Paternò–Büchi reaction. *Comprehensive Organic Synthesis* **1992**, *5*, 151-192.
71. Devanathan, S.; Ramamurthy, V. Consequences of hydrophobic association in photoreactions: photodimerization of alkyl cinnamates in water. *Journal of Photochemistry* **1987**, *40* (1), 67-77.
72. Dwars, T.; Paetzold, E.; Oehme, G. Reactions in micellar systems. *Angewandte Chemie International Edition* **2005**, *44* (44), 7174-7199.
73. Deraedt, C.; Astruc, D. Supramolecular nanoreactors for catalysis. *Coordination Chemistry Reviews* **2016**, *324*, 106-122.

74. Turro, N. J.; Grätzel, M.; Braun, A. M. Photophysical and photochemical processes in micellar systems. *Angewandte Chemie International Edition in English* **1980**, *19* (9), 675-696.
75. Fagnoni, M.; Albini, A. Photonucleophilic substitution reactions. *Organic Photochemistry and Photophysics* **2005**, 131-177.
76. Fukatsu, A.; Kondo, M.; Masaoka, S. Electrochemical measurements of molecular compounds in homogeneous solution under photoirradiation. *Coordination Chemistry Reviews* **2018**, *374*, 416-429.
77. Fischer, M. Industrial applications of photochemical syntheses. *Angewandte Chemie International Edition in English* **1978**, *17* (1), 16-26.
78. Myers, D. *Surfactant science and technology*; John Wiley & Sons, 2020.
79. Gyani Devi, Y.; Koya Pulikkal, A.; Gurung, J. Research progress on the synthesis of different types of gemini surfactants with a functionalized hydrophobic moiety and spacer. *ChemistrySelect* **2022**, *7* (45), e202203485.
80. Gilbert, M. Aliphatic polyamides. In *Brydson's Plastics Materials*, Elsevier, 2017; pp 487-511.
81. Peters, E. N. Engineering thermoplastics—materials, properties, trends. In *Applied plastics engineering handbook*, Elsevier, 2017; pp 3-26.