



# GREEN CHEMISTRY

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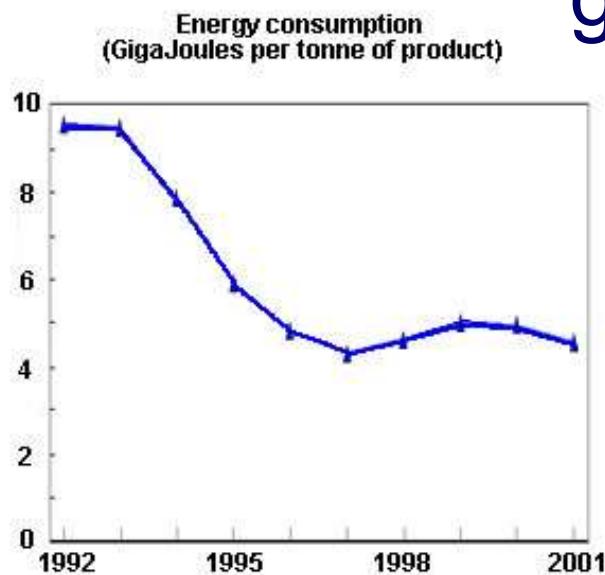
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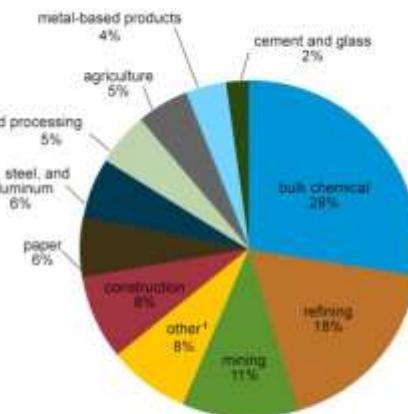


**Monitoring, control and maintenance**  
**Loss prevention**  
**Waste heat recovery**  
**Matching energy sources to requirements**

# Highly efficient synthetic techniques to achieve green process



U.S. Industrial sector energy consumption by type of industry, 2017



Note: Includes electricity purchases and energy sources used as feedstocks for making products. <sup>1</sup>Other includes wood products (1%), plastics products (1%), and all others (5%).  
Source: U.S. Energy Information Administration, Annual Energy Outlook 2018, Tables 25-35, February 2018.



## Microwave Ovens



Household MW ovens

The Use of Microwave Ovens for Rapid Organic Synthesis R. Gedye et al., Tetrahedron Lett. 1996, 27, 279.

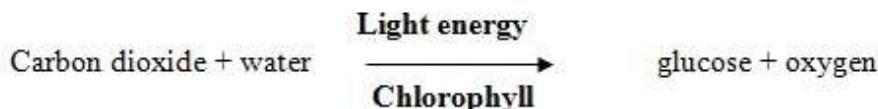


# Highly efficient synthetic techniques to achieve green process

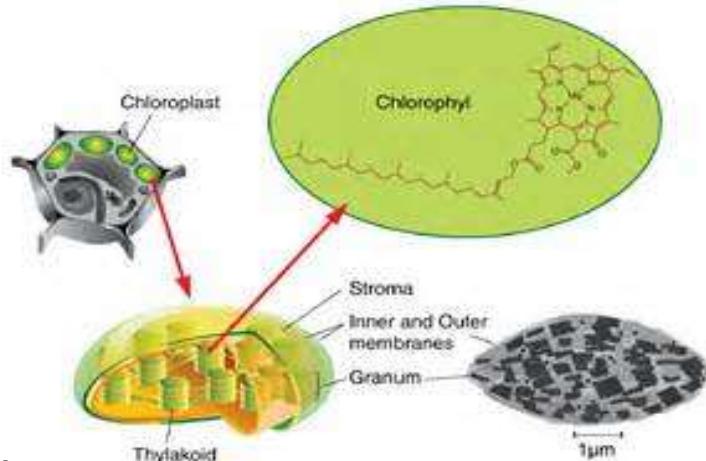
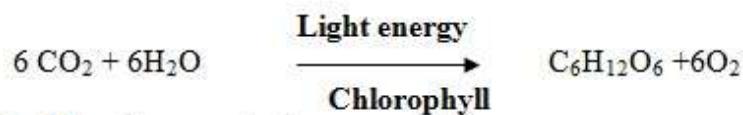
- Photochemical reactions
- Chemistry with microwaves
- Sonochemistry (ultrasound in synthetic chemistry)
- Electrochemical synthesis

# Photochemical reaction in nature

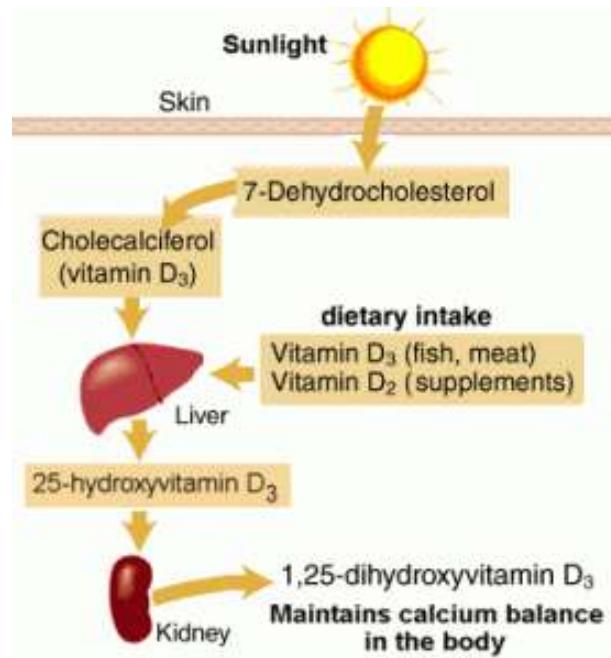
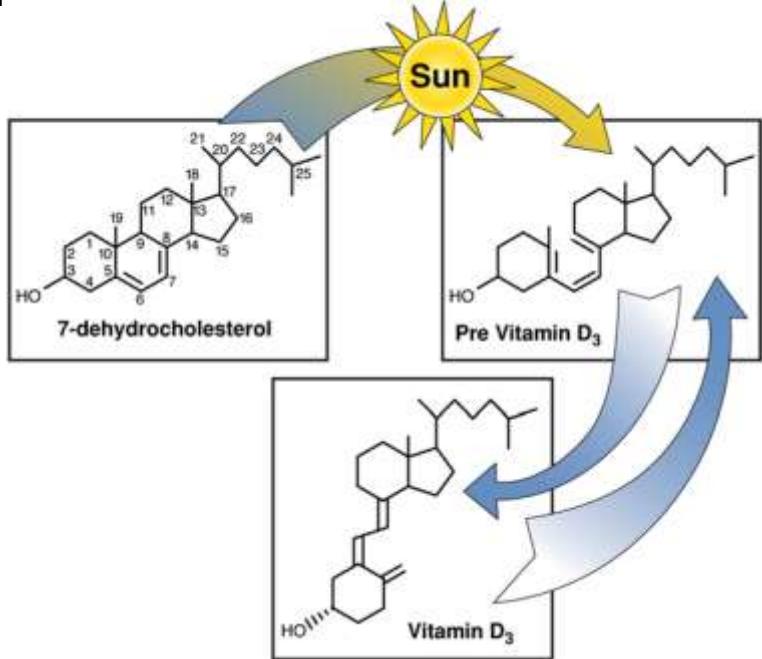
## Photosynthesis:



Balanced equation



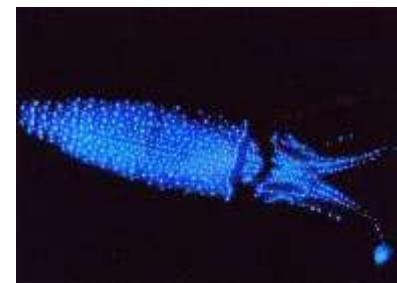
Plants use solar energy to convert carbon dioxide and water into glucose and oxygen.



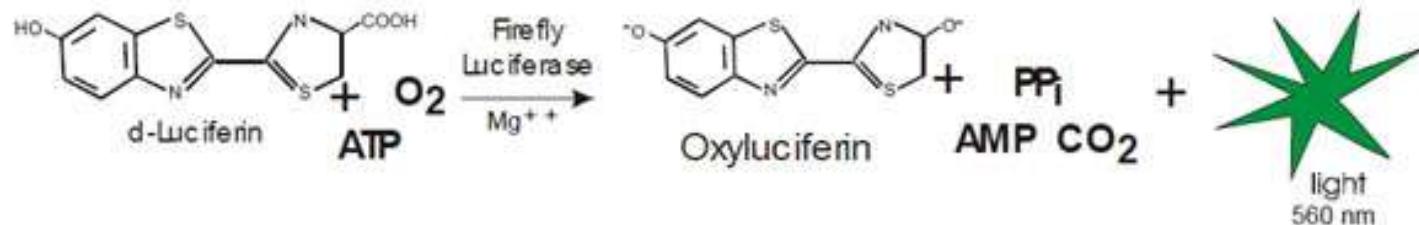
Formation of vitamin D<sub>3</sub> by exposure to sunlight in nature.

# Photochemical reaction in nature

## Bioluminescence:

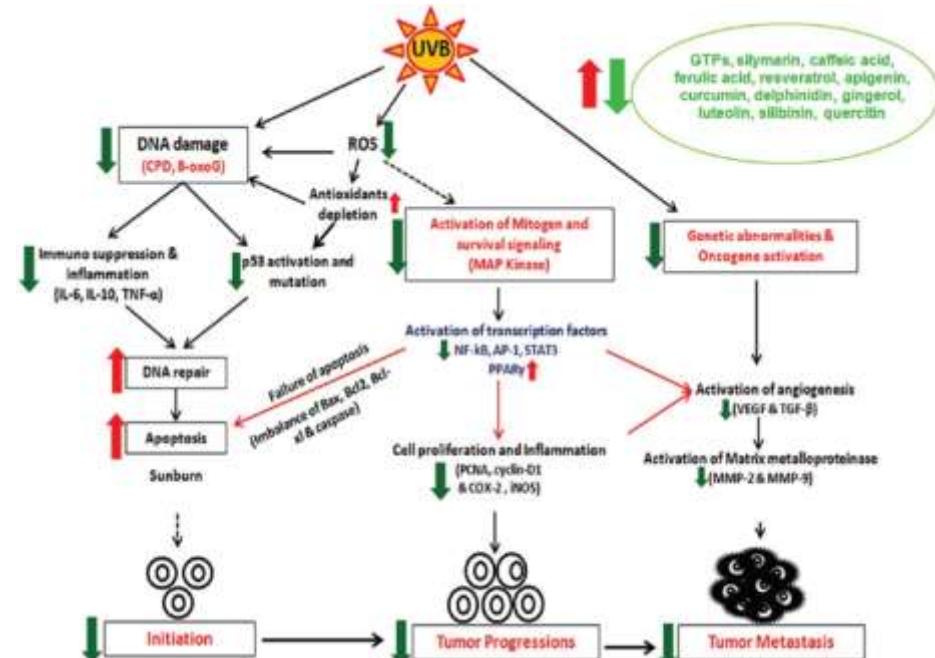
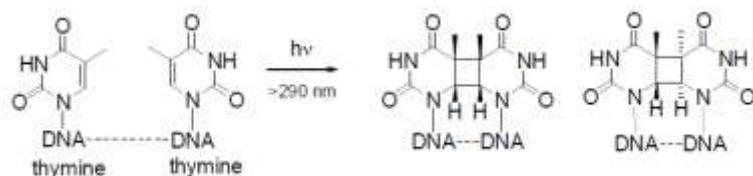


- Bioluminescence is a form of chemiluminescence where light energy is released by a chemical reaction.
- It occurs widely in marine vertebrates and invertebrates, as well as in some fungi, microorganisms.
- Fireflies, angler fish, and other organisms produce the light-emitting pigment **luciferin** and the enzyme **luciferase**. Luciferin reacts with oxygen to create light.

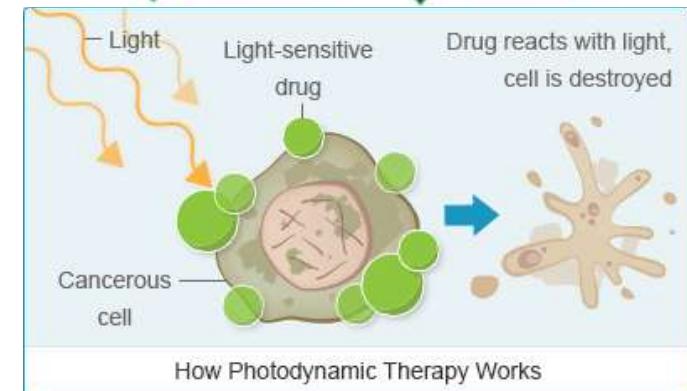
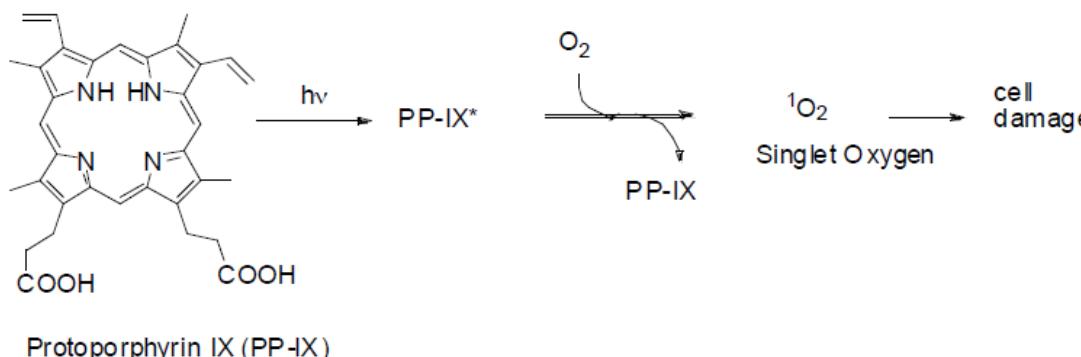


# Biological Effects of Solar Ultraviolet Radiation

## Photocarcinogenesis



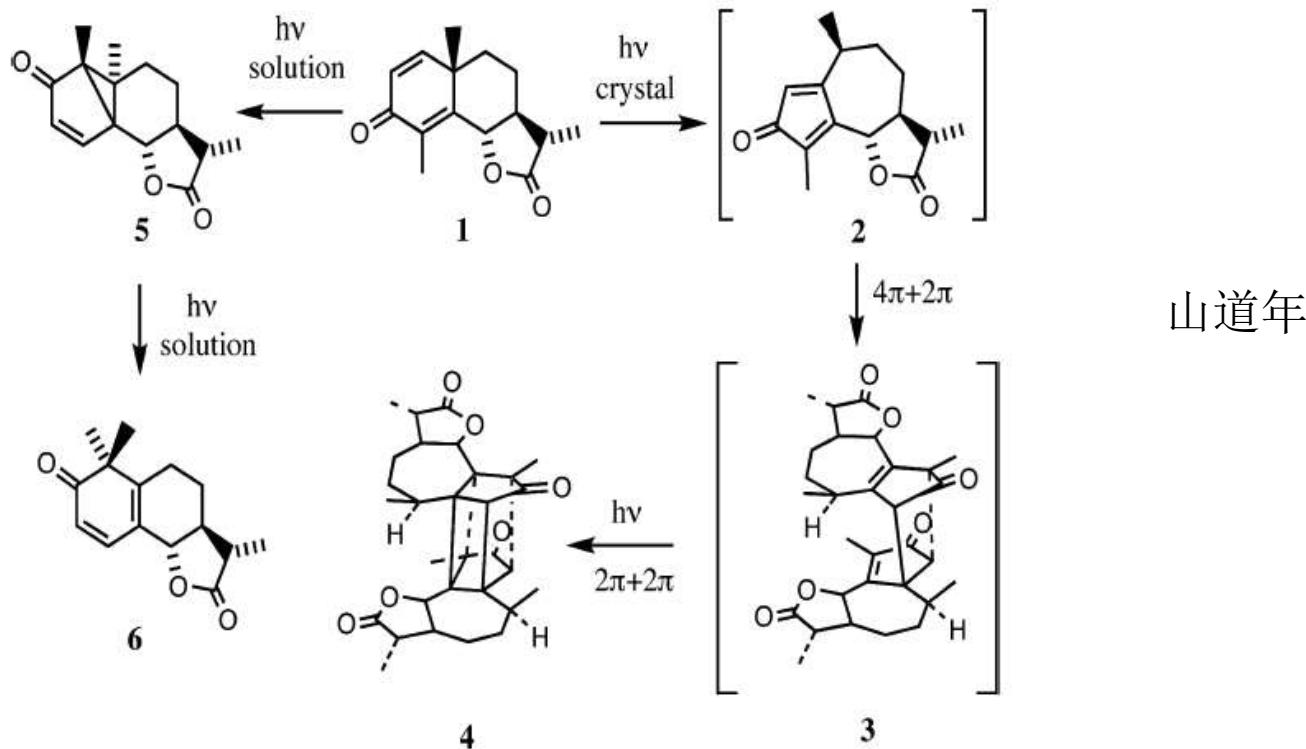
## Phototherapy



Light is used to destroy tumors by the action of **singlet oxygen** generated by photosensitized reactions of triplet oxygen. Typical photosensitizers include tetraphenylporphyrin and methylene blue. The resulting **singlet oxygen** is an aggressive oxidant, capable of converting C-H bonds into C-OH groups.

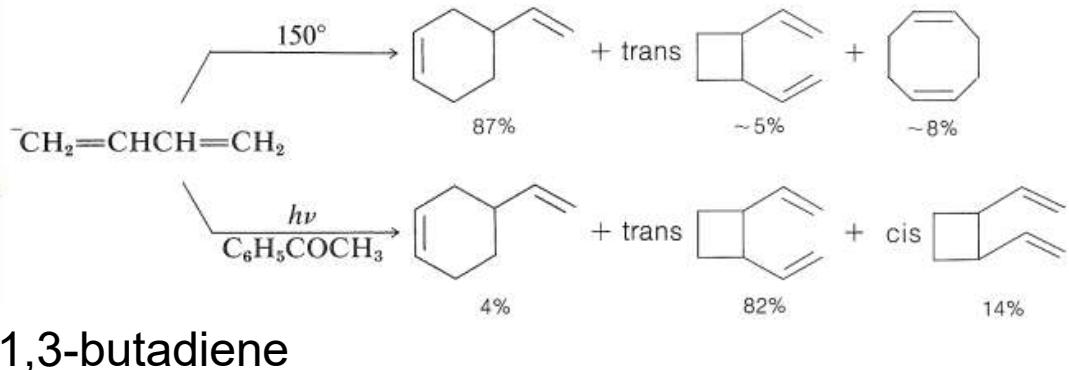
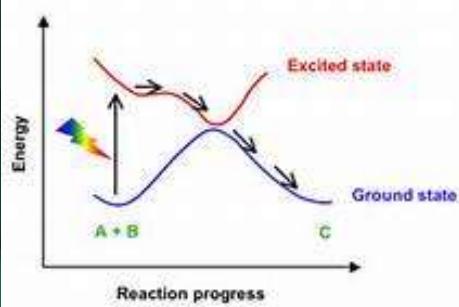
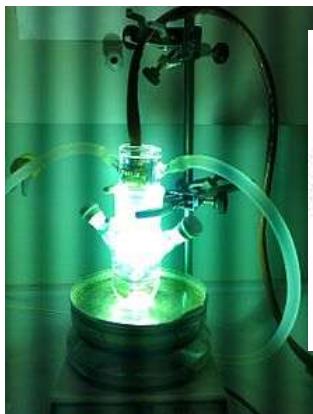
# The Beginnings of Organic Photochemistry

1834: First photochemical transformation described by Trommsdorff: Exposed  $\alpha$ -Santonin (1) crystals to sunlight and observed that they turned yellow and bursted.  
The mechanism was elucidated in 2007 by Arunkumar Natarajan et al.



The first step is a rearrangement reaction to a cyclopentadienone intermediate **2**, the second one a dimerization in a Diels-Alder reaction (**3**) and the third one an intramolecular [2+2]cycloaddition (**4**). The bursting effect is attributed to a large change in crystal volume on dimerization.

# Photochemical reactions

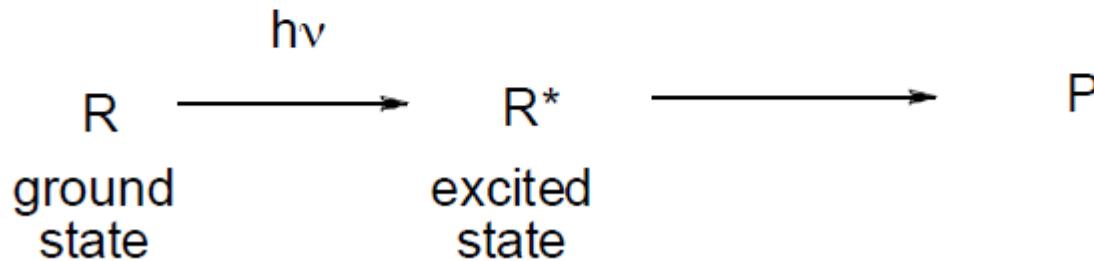


- **Photochemical reaction**, a chemical reaction initiated by the absorption of energy in the form of **light**.
- The consequence of molecules' absorbing light is the creation of **transient excited states** whose chemical and physical properties differ greatly from the original molecules.
- Photochemical paths access high energy intermediates that cannot be generated thermally, thereby overcoming large activation barriers **in a short period of time**, and allowing reactions otherwise **inaccessible by thermal processes**.

# Photochemical reactions

## Grotthus-Draper Law (First Law of Photochemistry)

*“Only radiation absorbed in a system can produce a chemical change.”*

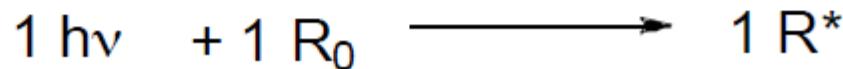


**Grotthuss–Draper law:** Light must be absorbed by a chemical substance in order for a photochemical reaction to take place.

# Photochemical reactions

## Stark-Einstein Law of Photochemical Equivalence

*“Number of activated molecules = number of quanta of radiation absorbed.”*



- **Stark-Einstein law:** Each photon of light absorbed by a chemical system, no more than one molecule is activated for a photochemical reaction, as defined by the quantum yield.

## Excited State of the Molecule

- Energy of the molecule has increased by the energy of the absorbed photon
- Photochemistry deals in part with properties of the excited state

$$E_{\text{exc}} = E^* - E_0 = h\nu = hc/\lambda$$

$E_{\text{exc}}$  = electronic excitation energy

$E^*$  = energy of excited state

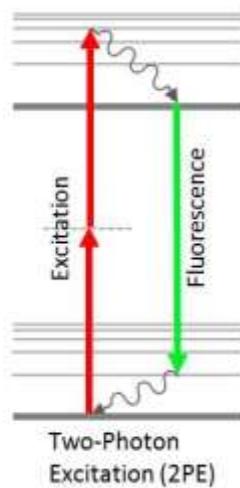
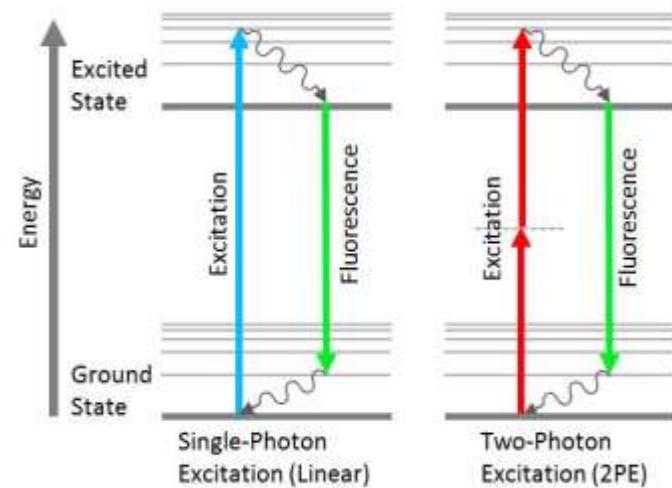
$E_0$  = energy of ground state

$h$  = Planck's constant

$\nu$  = frequency of absorbed radiation

$c$  = speed of light

$\lambda$  = wavelength of absorbed radiation



- Wavelength range of most photochemical reactions:

UV/Vis region:  $200 \text{ nm} \leq \lambda \leq 700 \text{ nm}$ ;  $143 \text{ kcal/mol} \geq E \geq 40.8 \text{ kcal/mol}$

With modern high intensity light sources (lasers) two photon excitation is possible (IR photolysis)

# Chromophore

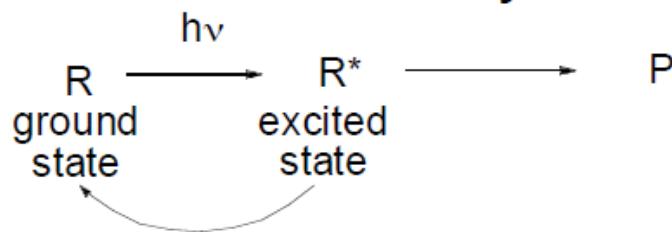
Electronic transitions involves a shift of one electrons from a lower to a higher energy molecular orbital. In most cases these molecular orbitals are associated with a specific part (e.g. functional group) of the molecule. *This part, that mainly absorbs the photon is termed the **chromophore**.*

Examples are aryl units, polyenes, and other pi-bonds, carbonyl,  $\text{-NO}_2$ ,  $\text{-N}_3$  and C-Hal groups.

*Absorption Characteristics of Some Common Chromophores*

Chromophore	Example	Solvent	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$	Type of transition
Alkene	$\text{C}_6\text{H}_{13}\text{HC}=\text{CH}_2$	<i>n</i> -Heptane	177	13,000	$\pi \rightarrow \pi^*$
Alkyne	$\text{C}_5\text{H}_{11}\text{C}\equiv\text{C}-\text{CH}_3$	<i>n</i> -Heptane	178 196 225	10,000 2,000 160	$\pi \rightarrow \pi^*$ — —
Carbonyl	$\begin{array}{c} \text{O} \\    \\ \text{CH}_3\text{CCH}_3 \end{array}$ $\begin{array}{c} \text{O} \\    \\ \text{CH}_3\text{CH} \end{array}$	<i>n</i> -Hexane	186 280 180 293	1,000 16 Large 12	$n \rightarrow \sigma^*$ $n \rightarrow \pi^*$ $n \rightarrow \sigma^*$ $n \rightarrow \pi^*$
Carboxyl	$\begin{array}{c} \text{O} \\    \\ \text{CH}_3\text{COH} \end{array}$	Ethanol	204	41	$n \rightarrow \pi^*$
Amido	$\begin{array}{c} \text{O} \\    \\ \text{CH}_3\text{CNH}_2 \end{array}$	Water	214	60	$n \rightarrow \pi^*$
Azo	$\text{H}_3\text{CN}=\text{NCH}_3$	Ethanol	339	5	$n \rightarrow \pi^*$
Nitro	$\text{CH}_3\text{NO}_2$	Isooctane	280	22	$n \rightarrow \pi^*$
Nitroso	$\text{C}_4\text{H}_9\text{NO}$	Ethyl ether	300 665	100 20	— $n \rightarrow \pi^*$
Nitrate	$\text{C}_2\text{H}_5\text{ONO}_2$	Dioxane	270	12	$n \rightarrow \pi^*$

# Photochemistry



**Properties of Excited State:** geometry; electronic configuration

## Photophysical Processes

### 1) Relaxation Processes

-Dissipation of energy and change of electronic configuration after excitation

Vibrational Relaxation

Internal Conversion

Intersystem Crossing

## Photochemical Processes

- Chemical reactions of the excited state  
fragmentations  
cis/trans isomerizations  
rearrangements  
addition/cyclization reactions  
photo oxidations

### 2) Decay Processes

-Return to ground state with release of energy

Quenching – energy transfer

Fluorescence

Phosphorescence

Luminescence

## Important Compound Classes

alkenes, dienes & polyenes

aromatic compounds

carbonyl compounds

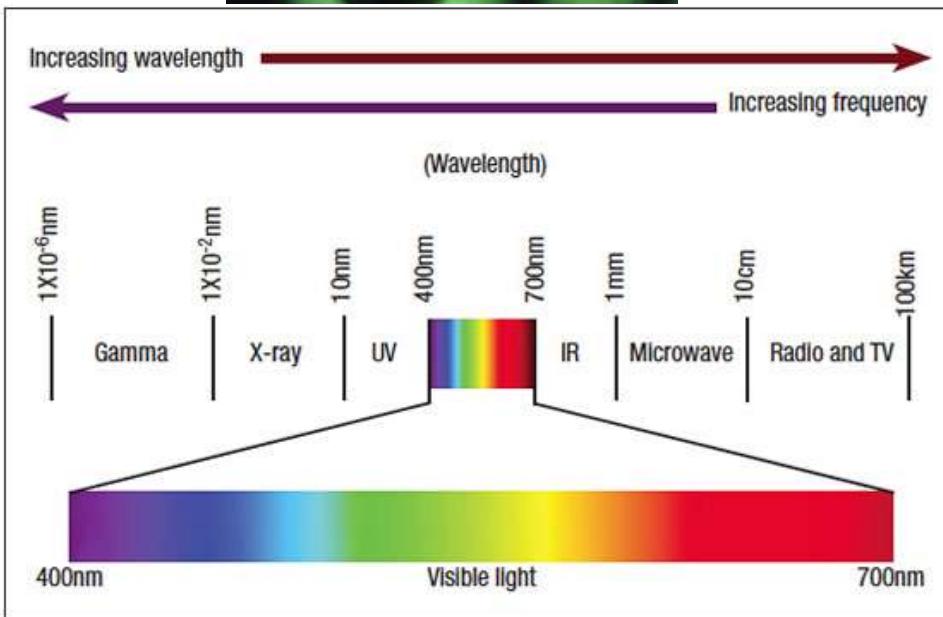
nitrogen-containing compounds

( $R-N_3$ ,  $RR'C=N_2$ ,  $R-NO_2$ ,  $R-N=N-R$ ,  $R-ONO$ )

singlet oxygen

halogen-containing compounds

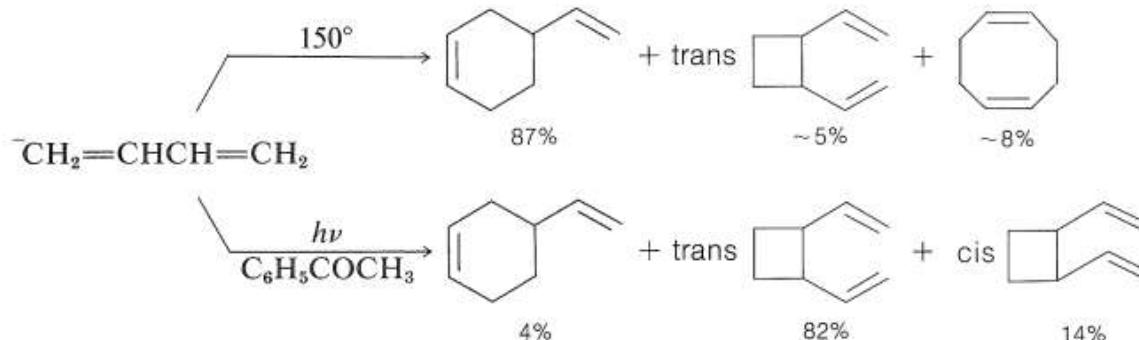
# Experimental set-up



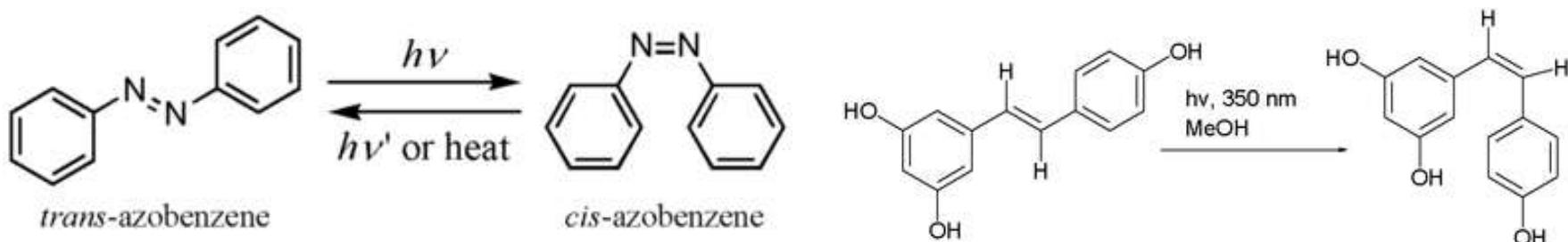
- A light source that emits wavelengths corresponding to an **electronic transition in the reactant**.
- Reactors: **Quartz** is used for the reactors as well as to contain the **lamp**. **Normal glassware** absorbs at wavelengths shorter than **275 nm**.
- Solvents: Different solvents can **absorb photons** of certain **wavelengths** to **prevent them** from reaching the substrate

# Advantages of and Challenges Faced by Photochemical Processes

- **Clean process:** Photons are very clean reagents, leaving no residues. A photo-initiated process therefore has potential advantages even when compared to reactions initiated by the use of catalysts.
- **Energy efficient:** Since the energy is more directed, reaction temperatures are generally low. This may give higher selectivity, by reducing by-product formation from competing reactions.
- **A unique way to prepare products that would be difficult to make by other routes.**



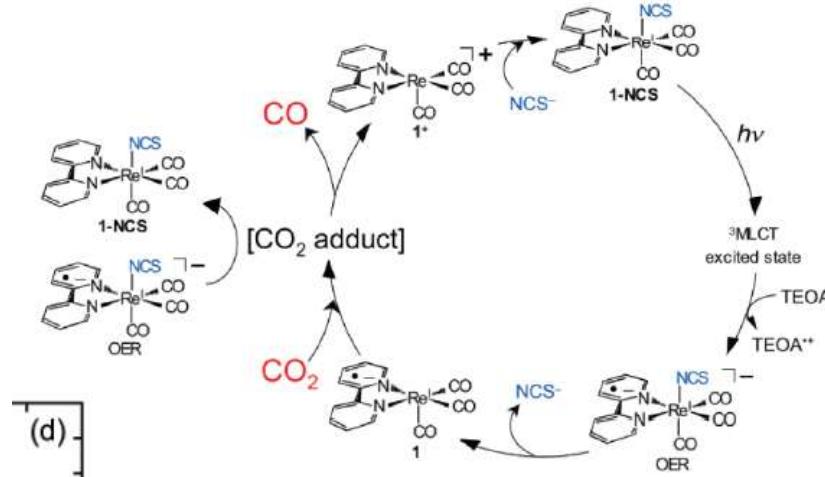
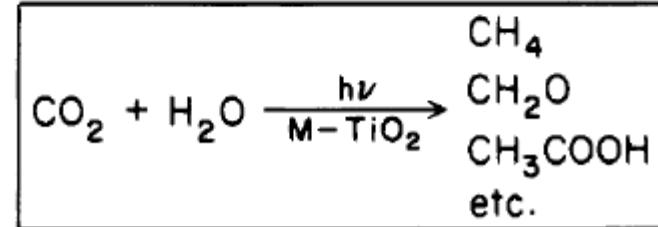
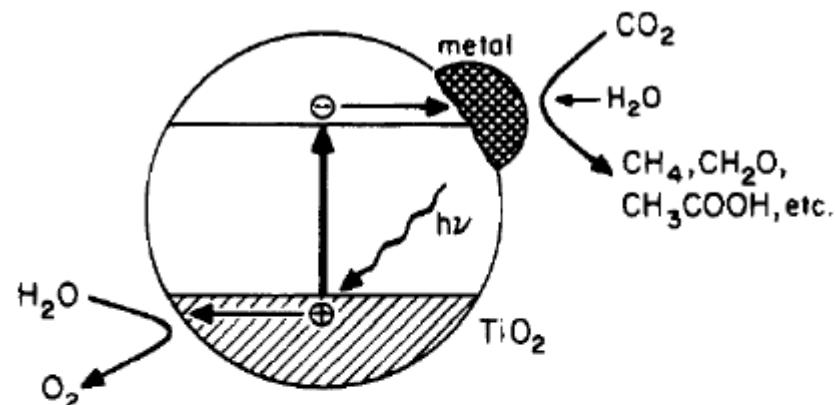
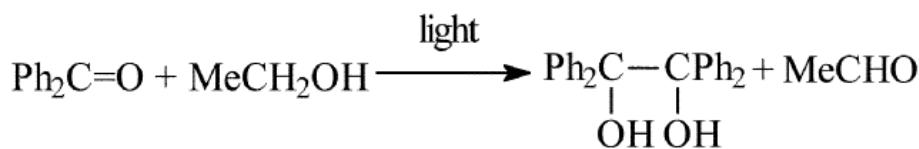
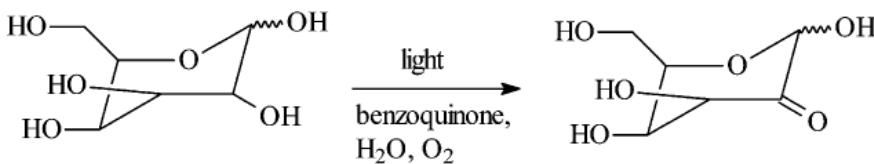
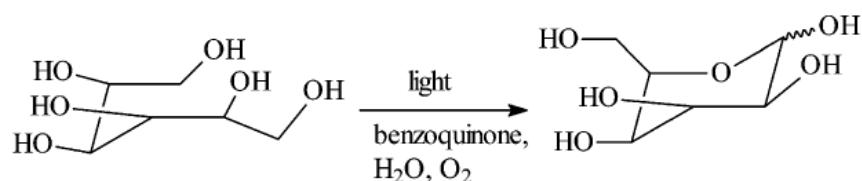
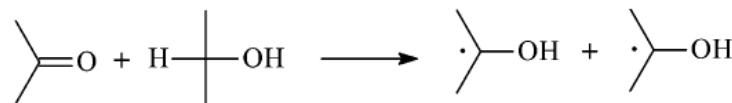
# Photoisomerization reaction



- **photoisomerization** is molecular behavior in which **structural change between isomers** is caused by **photoexcitation**.
- Both **reversible** and **irreversible isomerization** reactions exist. However, the word "photoisomerization" usually indicates a reversible process.
- Photoisomerizable molecules are already put to practical use, for instance, in **pigments for rewritable CDs, DVDs, and 3D optical data storage solutions**.
- In addition, recent interest in photoisomerizable molecules has been aimed at molecular devices, such as **molecular switches, molecular motors, and molecular electronics**.

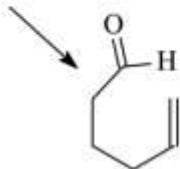
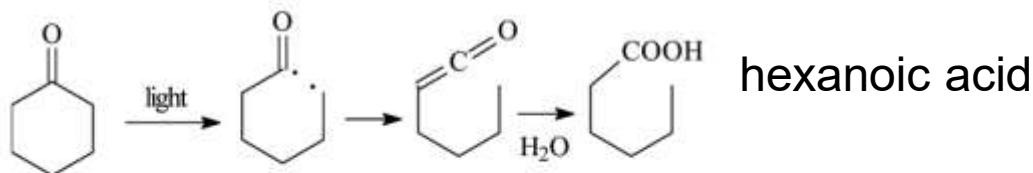
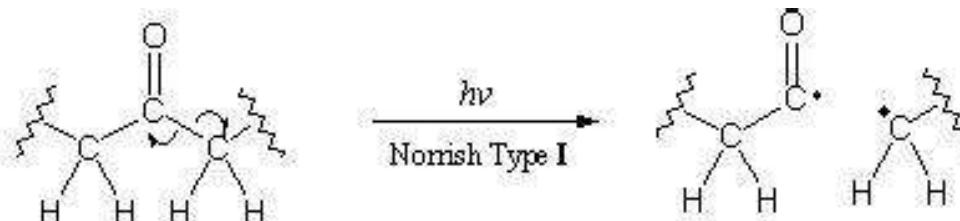
# Oxidations and reductions

Fast hydrogen abstraction by excited carbonyls generating radicals.

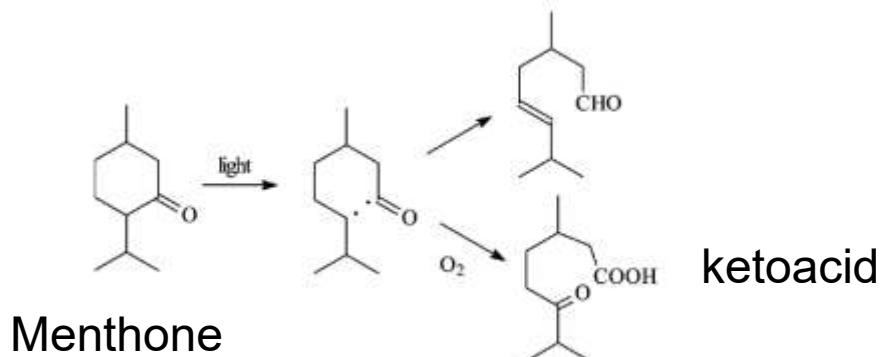


# Fragmentation reaction

Norrish I Type reaction

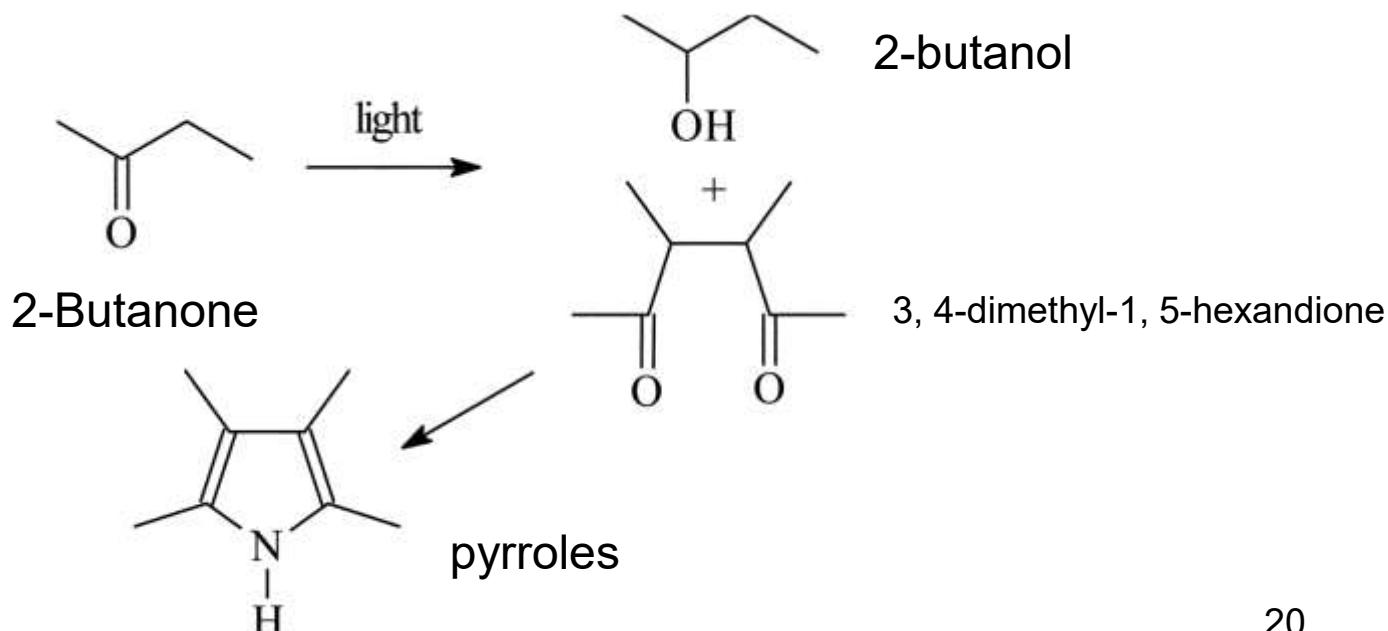
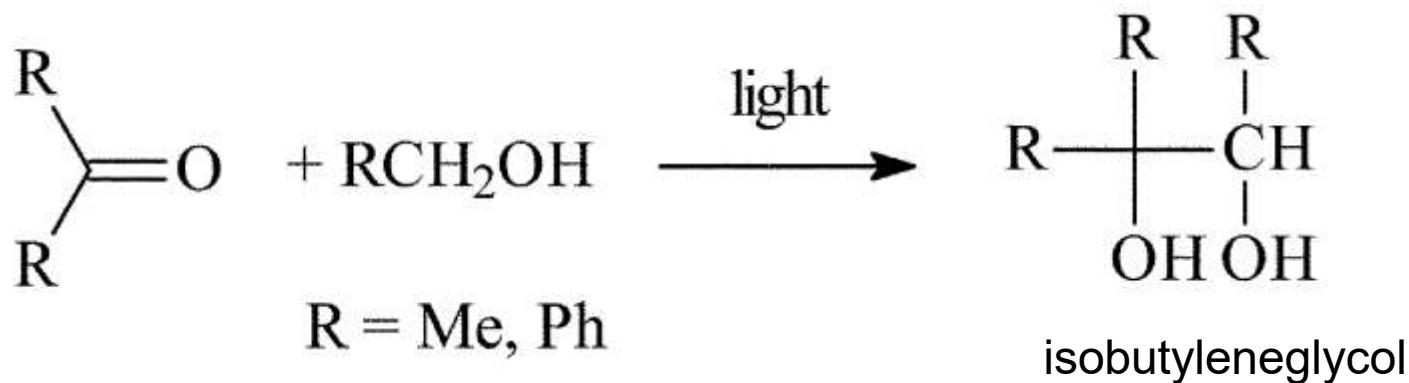


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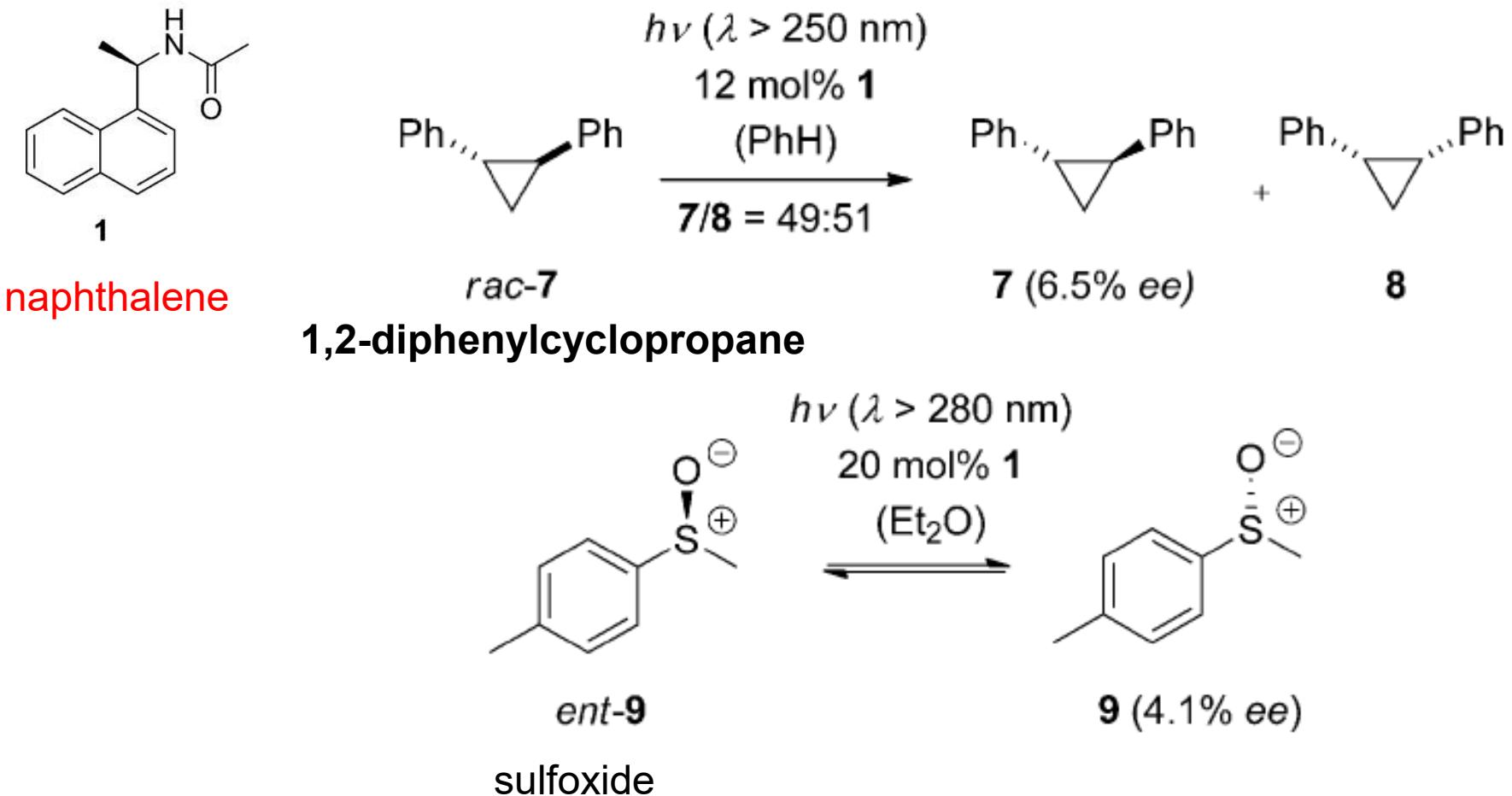


Menthone

# Condensation reactions

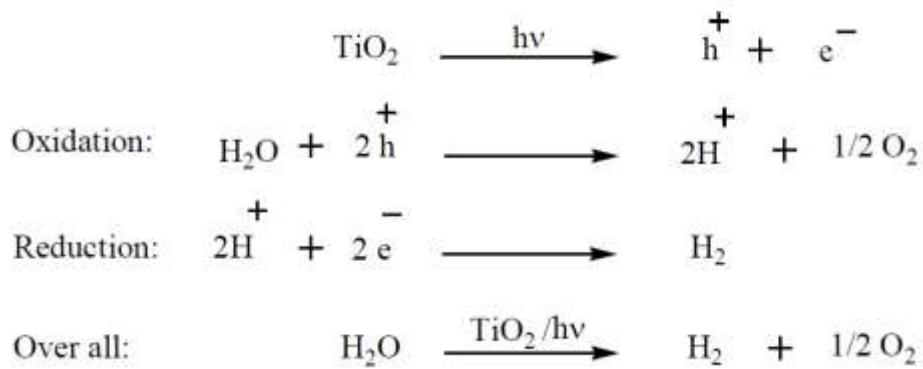
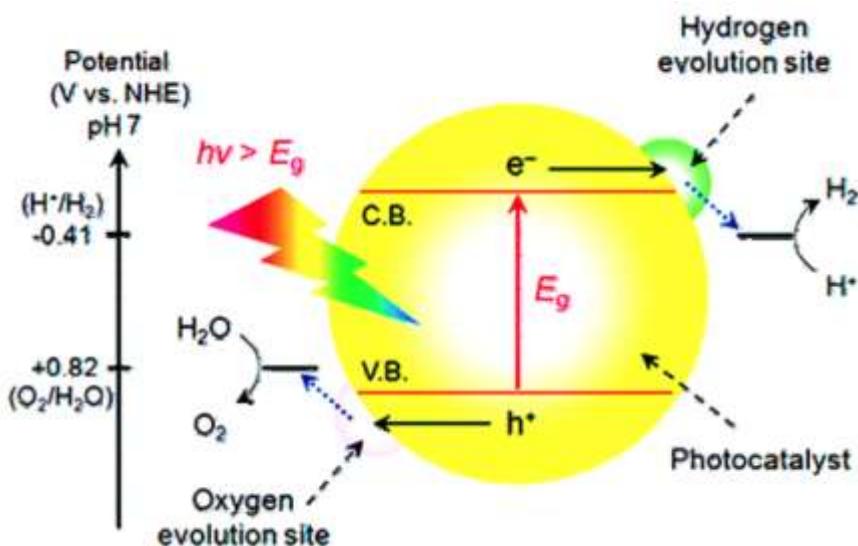


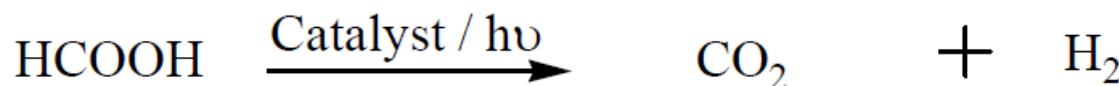
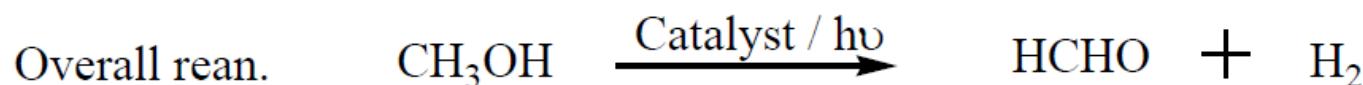
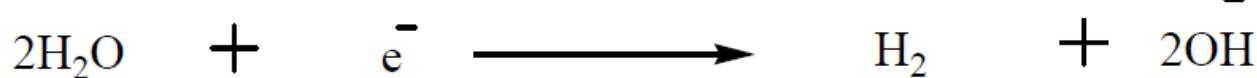
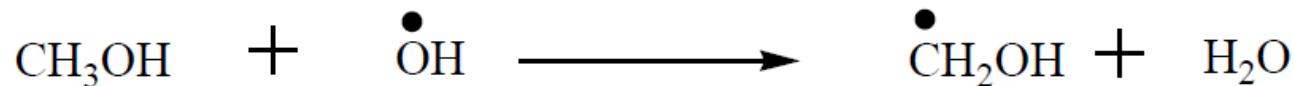
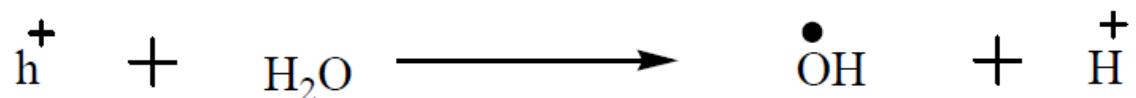
# Enantioselective Reactions



# photocatalyst

- In chemistry, **photocatalysis** is the acceleration of a photoreaction in the presence of a catalyst (e.g.,  $\text{TiO}_2$ ).
- The photocatalytic activity depends on the ability of the catalyst to create electron–hole pairs.
- Its practical application was made possible by the discovery of water electrolysis by means of titanium dioxide.

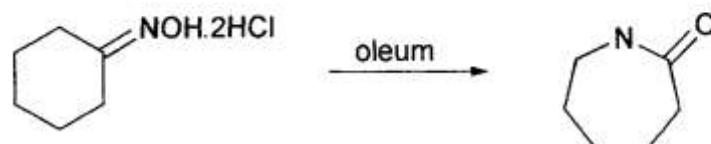
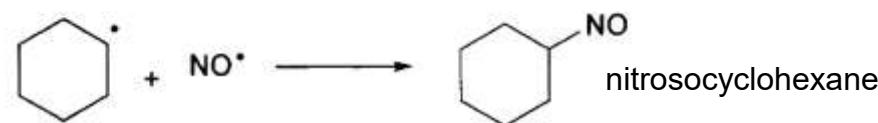
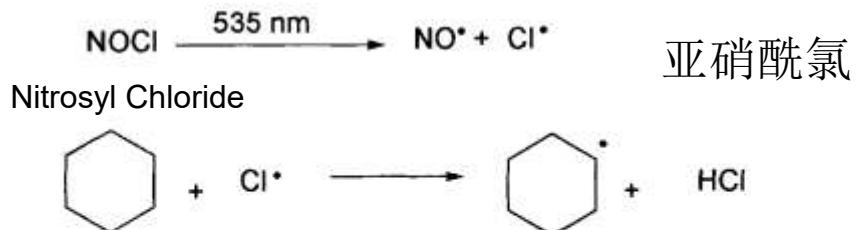
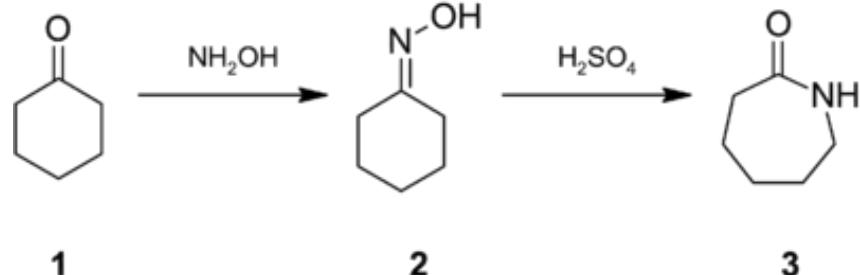
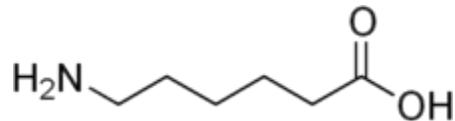




# Examples of Photochemical Reactions

Caprolactam (己内酰胺): World demand for caprolactam was estimated to reach 5 million tons per year for 2015

Conventional method

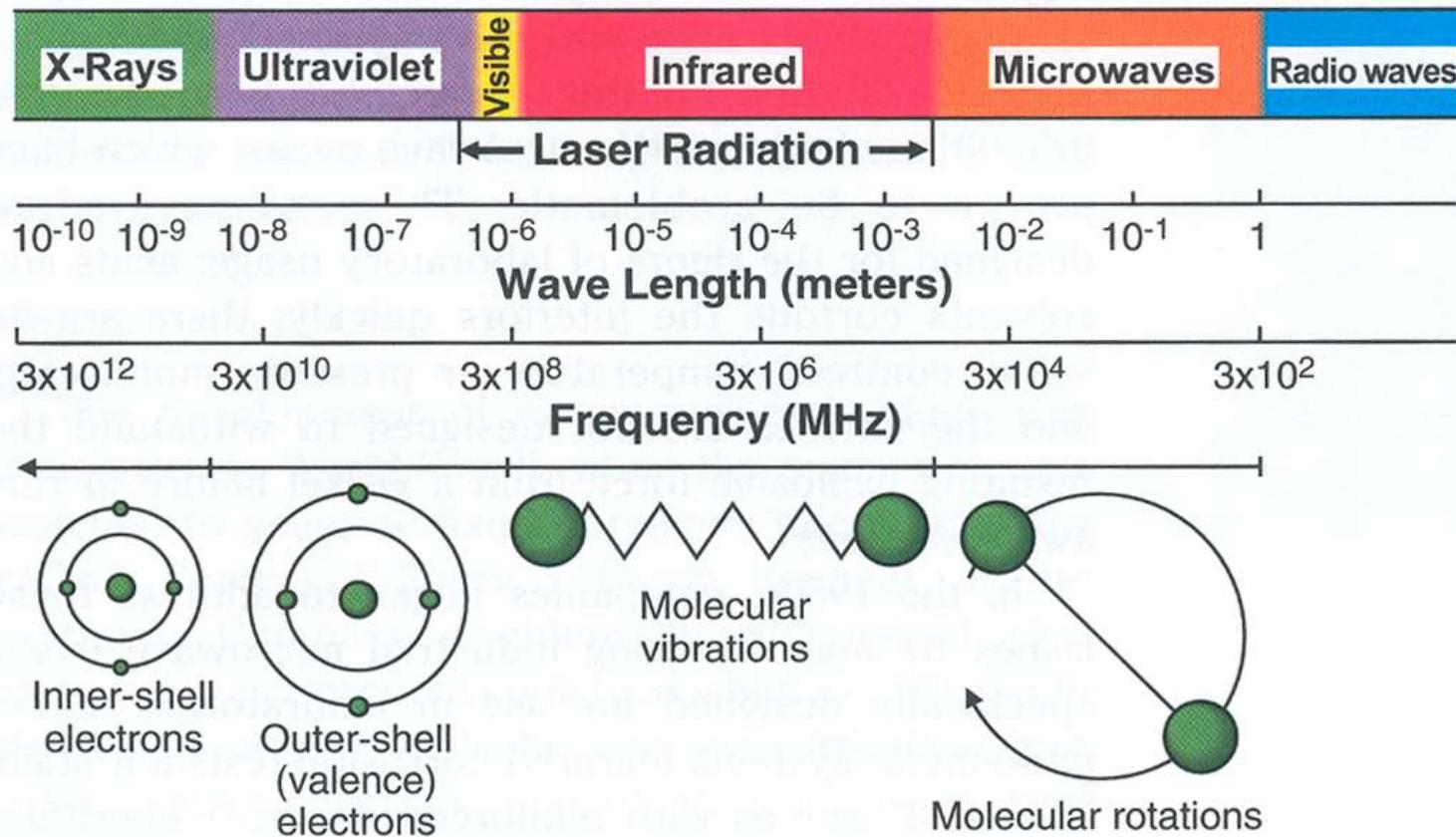


# Challenges Faced by Photochemical Processes

- Reactor fouling
- Light sources are polychromatic
- Light sources are expensive
- The power of transmitted light drops off easily

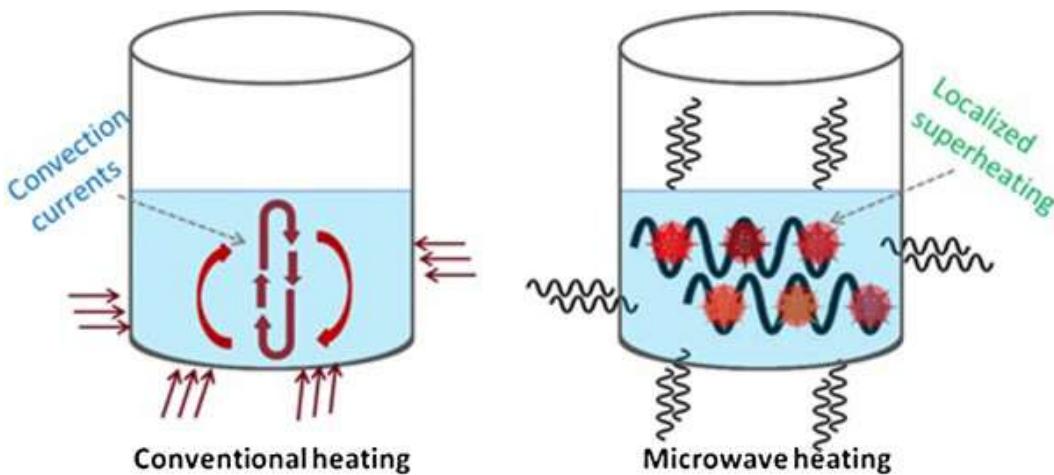
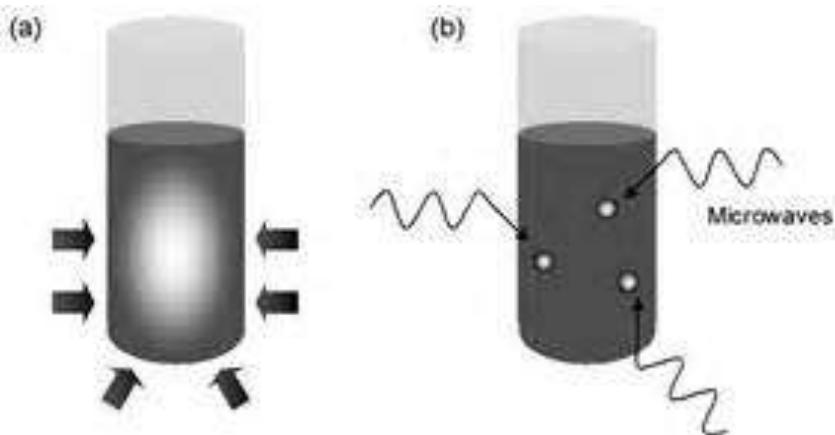
# Microwaves

The electromagnetic spectrum



- **Microwaves** are a form of electromagnetic radiation with wavelengths ranging from **1 meter** to **1 millimeter**; with frequencies between **300 MHz** and **300 GHz**.
- Its frequency can affect the behaviors of **rotations of molecules**.

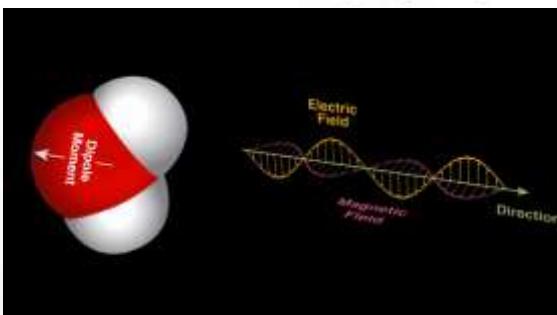
# Chemistry with microwaves



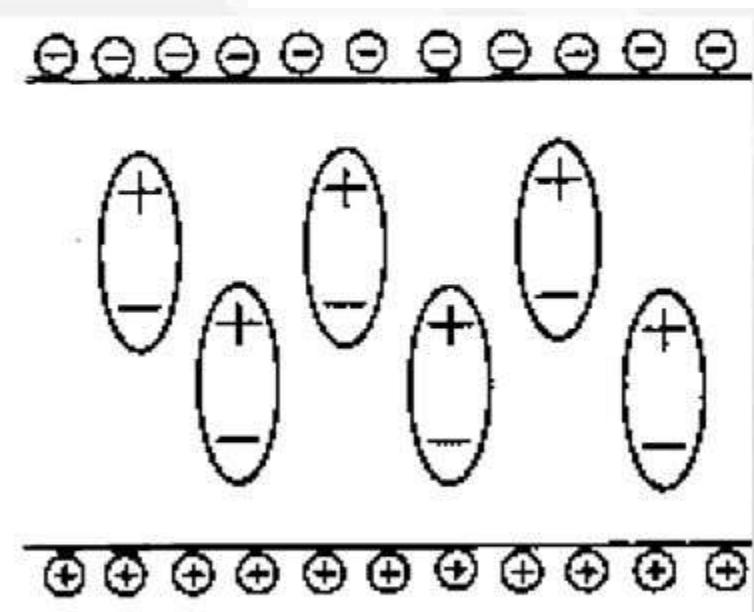
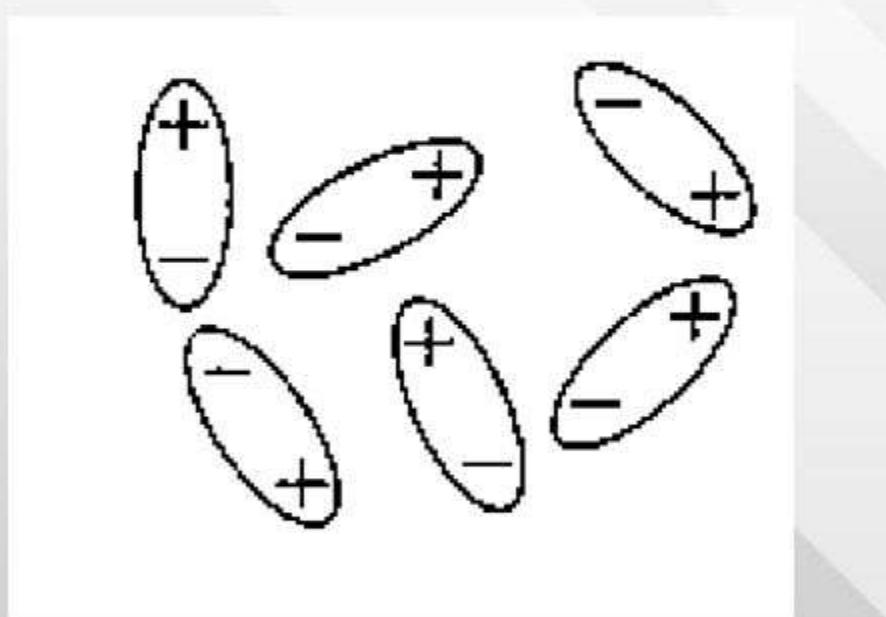
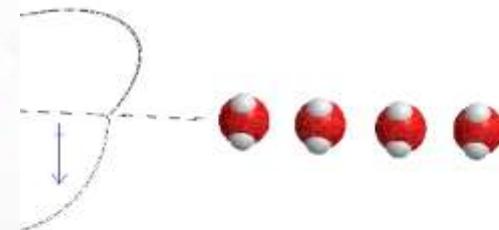
- Microwaves may be considered a more **efficient source of heating** than conventional **steam- or oil heated vessels** since the energy is **directly** imparted to the **reaction medium** rather than through the walls of a reaction vessel.

# *Mechanism of Microwave Heating*

[www.warlock.com.au](http://www.warlock.com.au)



## *Dipole Rotation*



Microwave heating occurs when the molecules become polarized by a alternating electromagnetic field. Rapid rotational movement of the molecules inside the materials cause collisions with neighboring molecules. The ensuing results is frictional heat.

# Chemistry with microwaves

- The **heating characteristics** of a particular material (for example, a solvent) are dependent on its **dielectric properties**.
- The **ability** of a substance to **convert electromagnetic energy** into **heat** is determined by the so-called **energy dissipation factor ( $\tan\delta$ )**.
- A reaction **medium** with a **high  $\tan\delta$**  value is required for **efficient absorption** and for **rapid heating**.

Loss Tangent (Energy Dissipation Factor) –  
a measure of the ability to absorb  
microwave energy and convert it into  
thermal energy (heat)

- Derived from Maxwell's eqn  
$$\tan\delta = \epsilon''/\epsilon'$$
- $\epsilon''$  = loss factor
- $\epsilon'$  = dielectric constant

**Table 1:** Loss factors ( $\tan\delta$ ) of different solvents.<sup>[a]</sup>

Solvent	$\tan\delta$	Solvent	$\tan\delta$
ethylene glycol	1.350	DMF	0.161
ethanol	0.941	1,2-dichloroethane	0.127
DMSO	0.825	water	0.123
2-propanol	0.799	chlorobenzene	0.101
formic acid	0.722	chloroform	0.091
methanol	0.659	acetonitrile	0.062
nitrobenzene	0.589	ethyl acetate	0.059
1-butanol	0.571	acetone	0.054
2-butanol	0.447	tetrahydrofuran	0.047
1,2-dichlorobenzene	0.280	dichloromethane	0.042
NMP	0.275	toluene	0.040
acetic acid	0.174	hexane	0.020

[a] Data from ref. [15]; 2.45 GHz, 20°C.

# Microwave-assisted Reactions



Advantage: With A heating rate of **10 °C per second**, the overall reaction time can be considerably **shortened**.

Shortcomings: Microwave experiments can raise **safety issues** due to the facts of **overheating and explosions**.

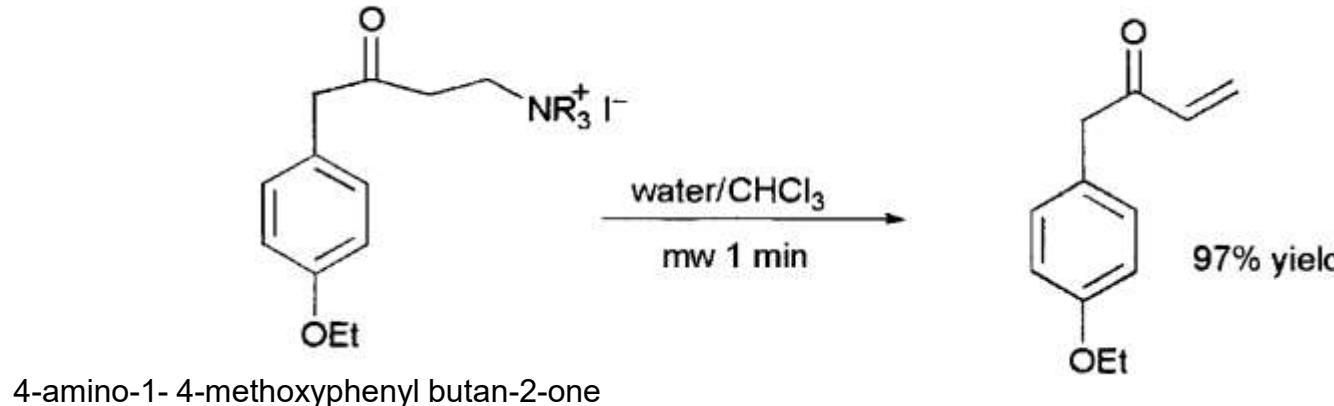
Challenges: The natural limitations on solvents imposed by microwave heating, has led to many reactions being carried out in **water** or, more commonly, under **solvent-free conditions**.

- Owing to their high polarity and non-volatility, **ionic liquids** might be ideal for carrying out high temperature reactions efficiently.



# Microwave-assisted Reactions

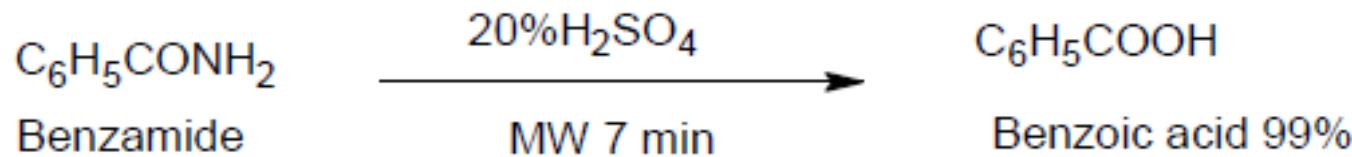
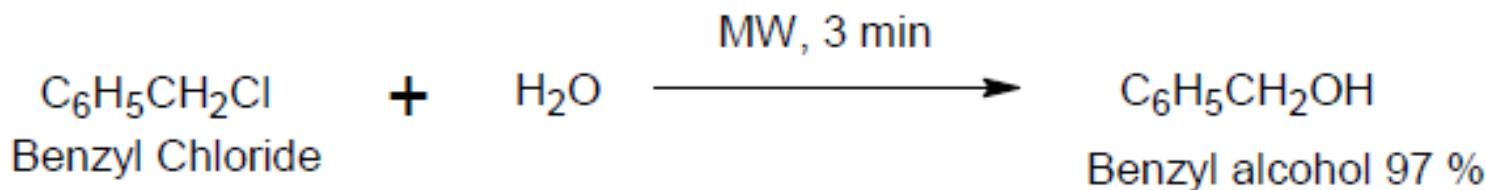
## Synthesis of a thermally unstable Hofmann elimination product



- The starting quaternary ammonium compound was water-soluble. Microwave irradiation **quickly heated** the water phase to over 100 °C, **causing rapid elimination** (reaction time, 1 min).
- The **less polar product** rapidly **partitioned into the chloroform phase**, which being less polar had only reached a temperature of **48 °C**.
- **This low temperature** enabled the product to be **isolated in 97% yield**, twice that using conventional heating.

# Microwave Assisted Reactions

# Hydrolysis

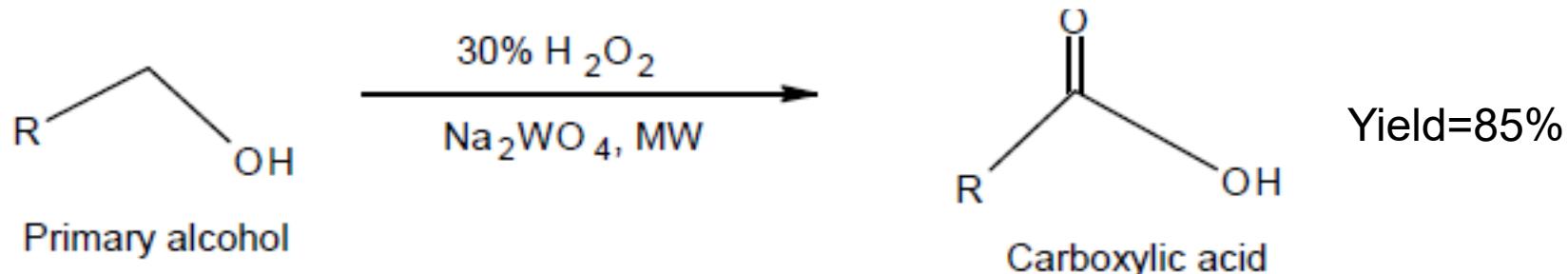


Quantitative conversion was achieved in **7 min** under microwave irradiation at **140 °C**, compared to a 90% conversion after a 1-h **reflux** using a conventional heating source.

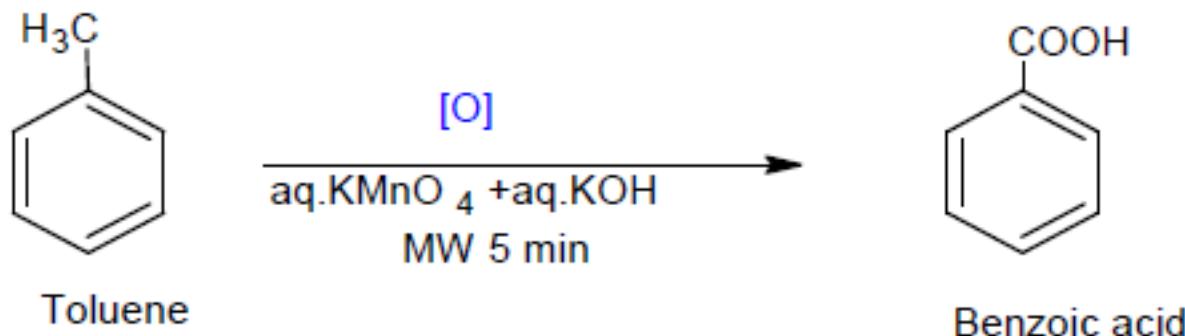
The difference in reaction time can be accounted for by the difference in reaction temperature coupled with the very rapid heating of the microwave reactor.

# Microwave Assisted Reactions

## Oxidation

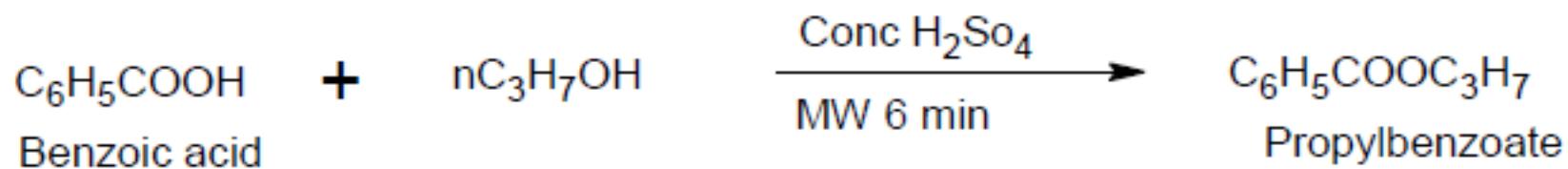


A range of primary alcohols have been oxidized to the corresponding carboxylic acids using sodium tungstate as catalyst in 30% aqueous hydrogen peroxide.



# Microwave Assisted Reactions

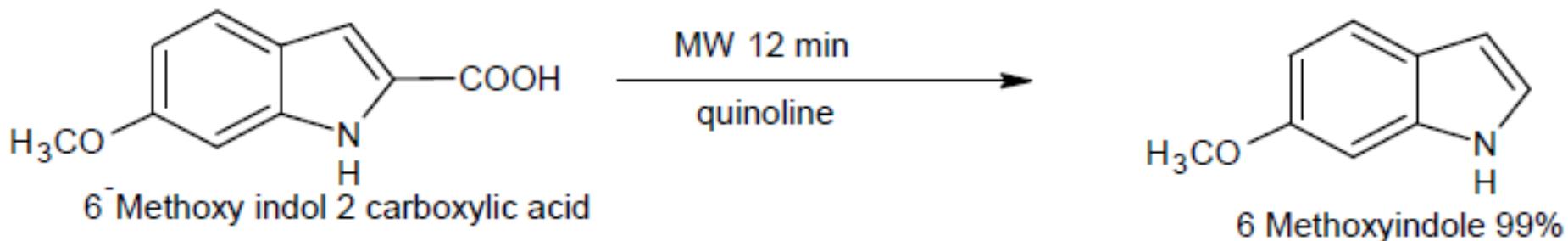
# Esterification



A mixture of benzoic acid and n- propanol on heating in a microwave oven for **6 min** in presence of catalytic amount of concentration of Sulfuric acid gives propylbenzoate.

# Microwave Assisted Reactions using Solvents

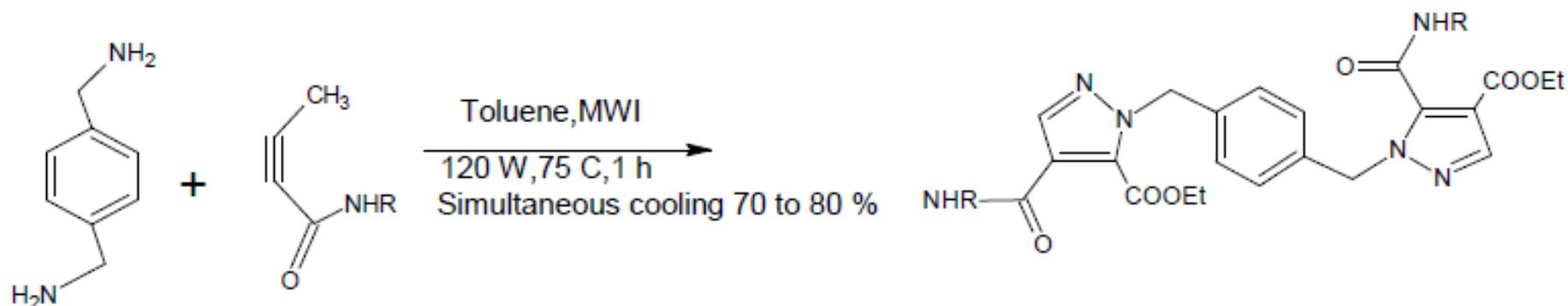
## Decarboxylation



Conventional **decarboxylation** of carboxylic acids involve **refluxing** in quinoline in presence of **copper chromate** and the yields are low. However, in the presence of microwaves decarboxylation takes place in much shorter time

# Microwave Assisted Reactions using Solvents

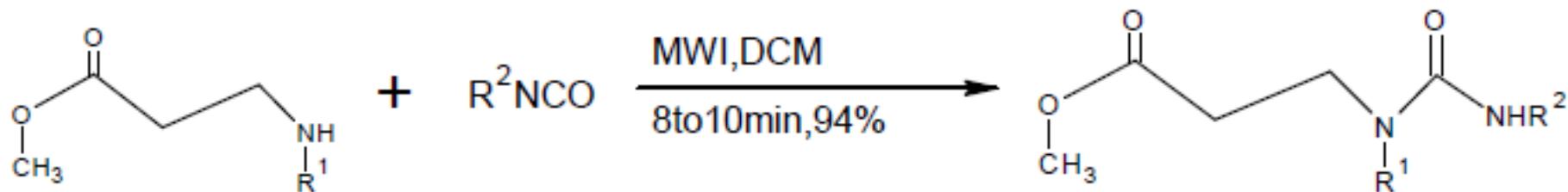
## Cycloaddition



Cycloadducts were prepared by carrying out the reaction between an azide and a substituted amine in toluene. This reaction was carried out under microwave irradiation at 120 W at 75 °C for 1 h. The product was isolated in 70–80 % yield.

# Microwave Assisted Reactions using Solvents

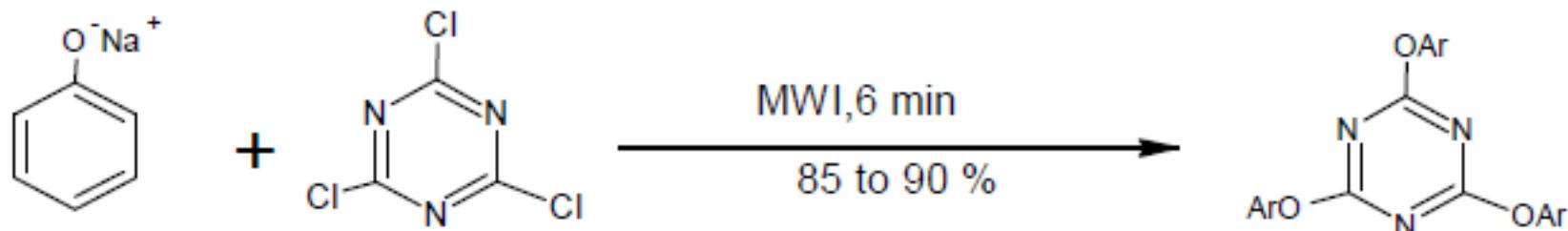
## N-Acylations



N-Acylations were carried out using secondary amines and isocyanate in dichloromethane under microwave irradiation (8–10 min), yielding the product in 94% yield.

# Microwave assisted Reactions under Solvent-Free Conditions

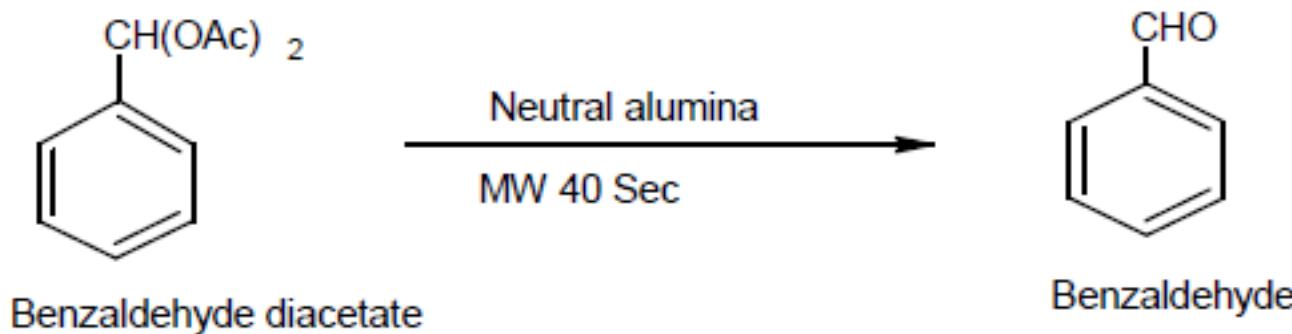
## Aromatic Nucleophilic Substitutions



Formation of substituted triazines aromatic nucleophilic substitutions are carried out using sodium phenoxide and 1,3,5-trichlorotriazine under microwave irradiation (6 min). The products, 1,3,5-triaryloxytriazines are obtained in 85–90% yields

# Microwave assisted Reactions under Solvent-Free Conditions

## Deacetylation



- Aldehydes, phenol and alcohols are protected by acetylation. After the reaction, the deacetylation of the product is carried out usually under **acidic or basic conditions** the process takes **long time** and the **yields are low**.
- Use of microwave irradiation reduces the time of deacetylation and **the yields are good**.

## **Advantages**

- Rapid reactions
- High purity of products
- Less side-products
- Improved yields
- Simplified and improved synthetic procedure
- Wider usable range of temperature
- Higher energy efficiency
- Sophisticated measurement and safety technology
- Modular systems enable changing from mg to kg scale.

## **Disadvantages**

- Heat force control is difficult
- Water evaporation
- Closed container is dangerous because it could be burst

# Ultrasound



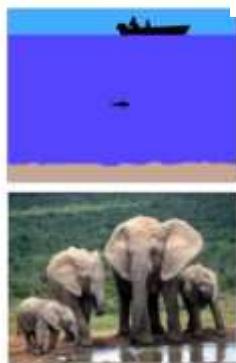
## Ultrasound and Infrasound

**Ultrasound** is high frequency sound, above 20 000 Hz, too high to be heard by humans.

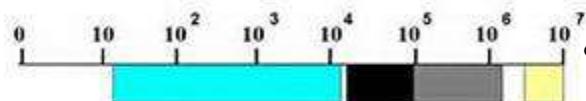
Ultrasound echoes can be used to measure distance (e.g. sonar) and to see inside objects (scans).

**Infrasound** is low frequency sound, inaudible to human, although we may feel the very slow vibrations.

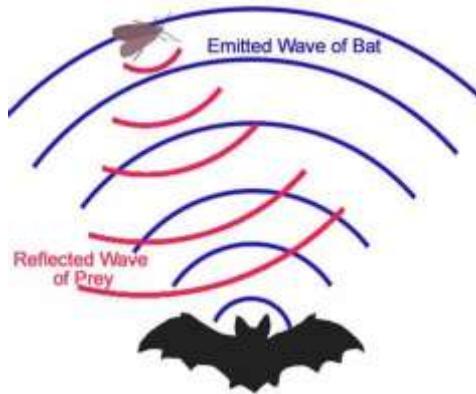
Earthquake waves are a form of infrasound. Elephants and some other large animals can hear infrasound.



## THE FREQUENCY RANGES OF SOUND



Human hearing	16Hz - 18kHz
Conventional power ultrasound	20kHz - 100kHz
Extended range for sonochemistry	20kHz - 2MHz
Diagnostic ultrasound	5MHz - 10MHz

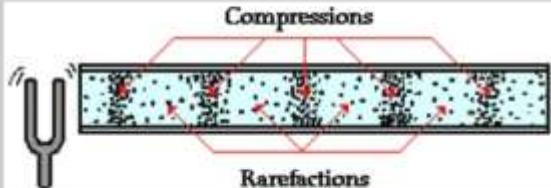


- Ultrasound refers to sound waves with frequencies higher than those detectable by the human ear, i.e. around **18 kHz**.
- The ultrasound frequencies of interest for chemical reactions (typically **20-100 kHz**) are much lower than used for medical applications (**3-10 MHz**).



# Ultrasound

## Sound is a pressure wave

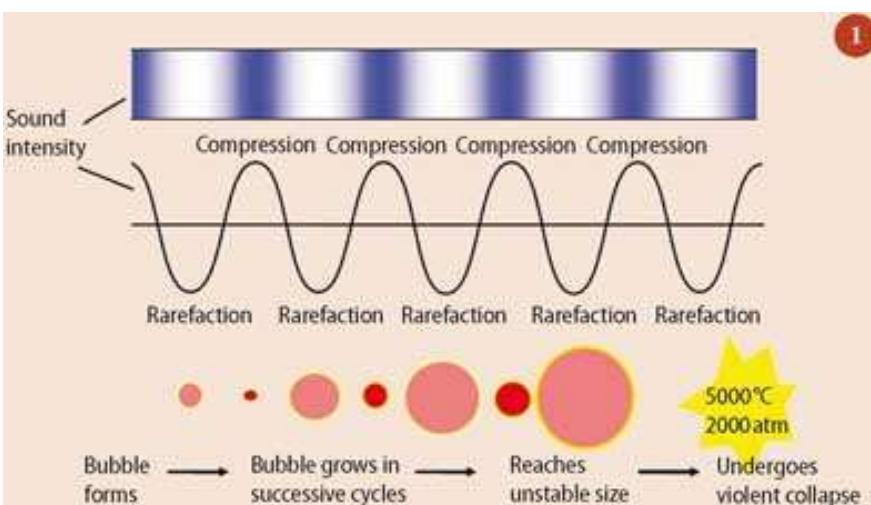


**Compressions** are regions of high air pressure.

**Rarefactions** are regions of low air pressure.

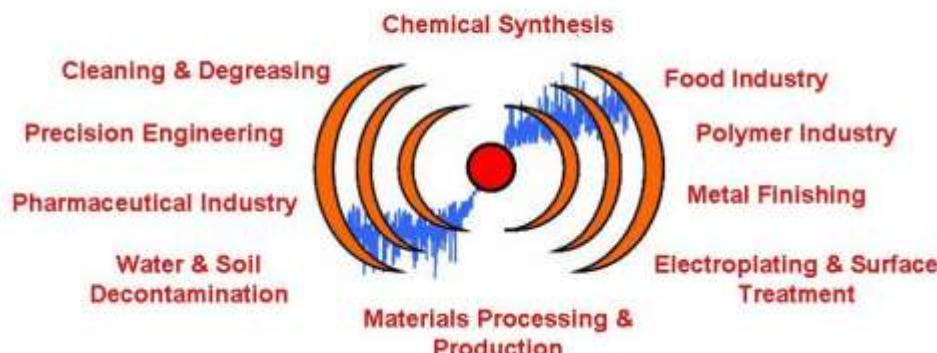
The diagram below depicts a sound wave created by a tuning fork and propagated through the air in an open tube.

- A sound wave is propagated by a series of compression and rarefaction cycles. When it passes through a liquid medium, it causes the molecules to oscillate around their mean position, **the average distance between molecules is reduced and, conversely, it is increased during rarefaction.**



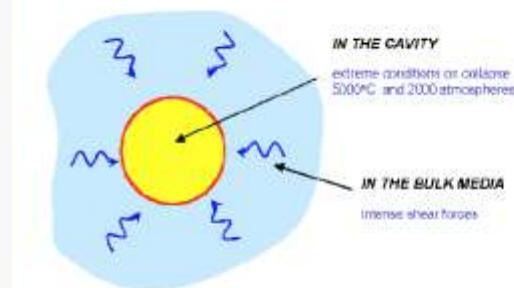
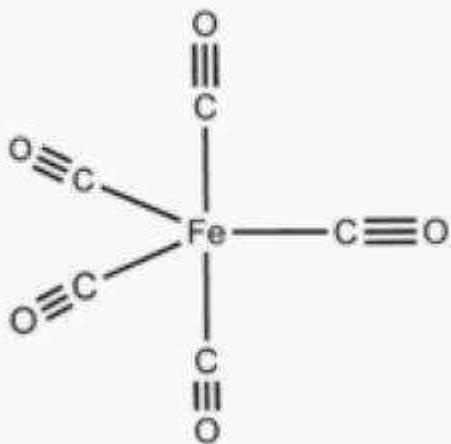
## INDUSTRIAL SONOCHEMISTRY

### Applications

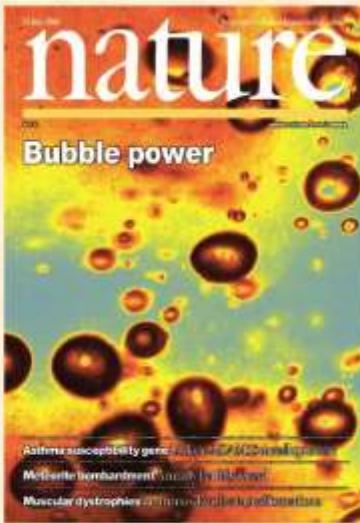


- Under appropriate conditions in the rarefaction cycle, the attractive forces of the molecules of the liquid may be overcome, causing bubbles to form. **If the internal forces are great enough to cause collapse of these bubbles very high local temperatures (around 5000 °C) and pressures (over 1000 bar) may be created.**

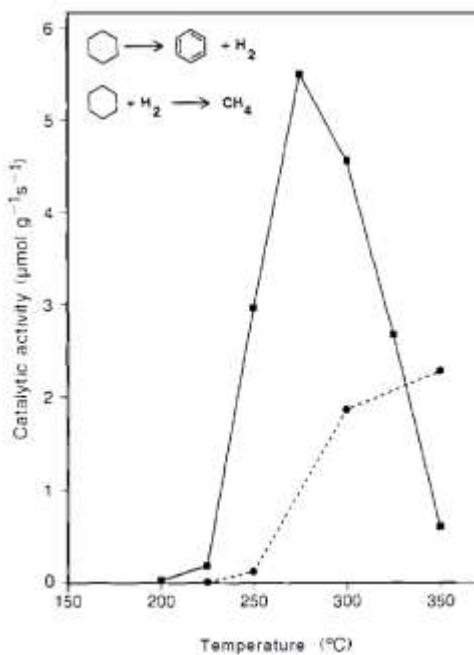
## Iron pentacarbonyl



Acoustic cavitation in a homogeneous liquid

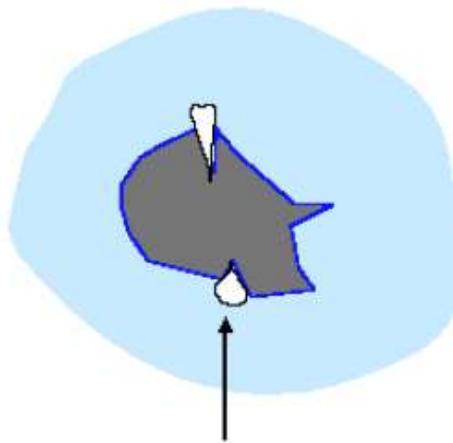


Suslick - ~ 4-5000 K



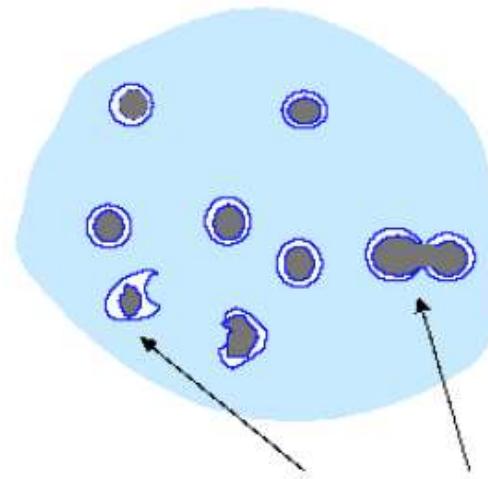
# Ultrasonics/Sonochemistry – Acoustic Cavitation

LARGE PARTICLES



surface cavitation due to defects  
leading to **fragmentation**

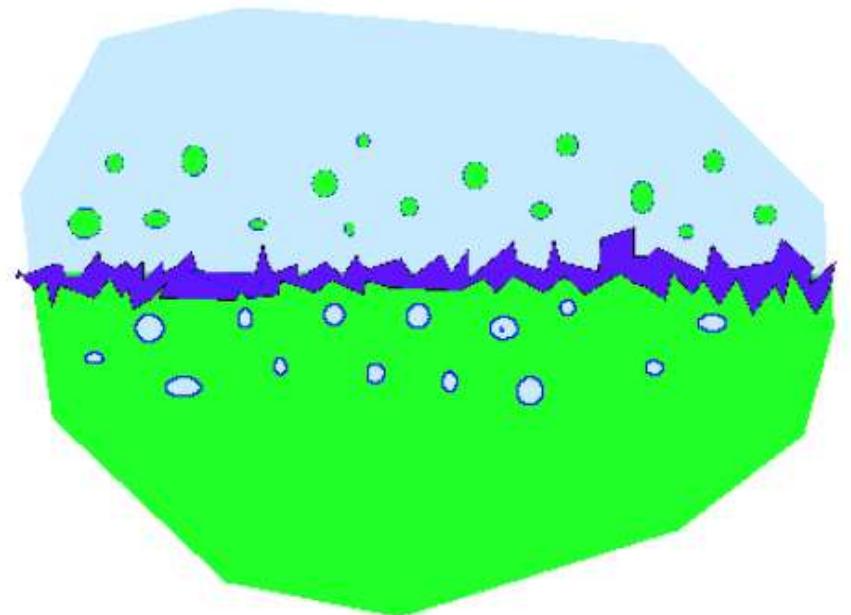
SMALL PARTICLES



collision can lead to **surface erosion** or **fusion**

Acoustic cavitation in solid/liquid system

# Ultrasonics/Sonochemistry – Acoustic Cavitation



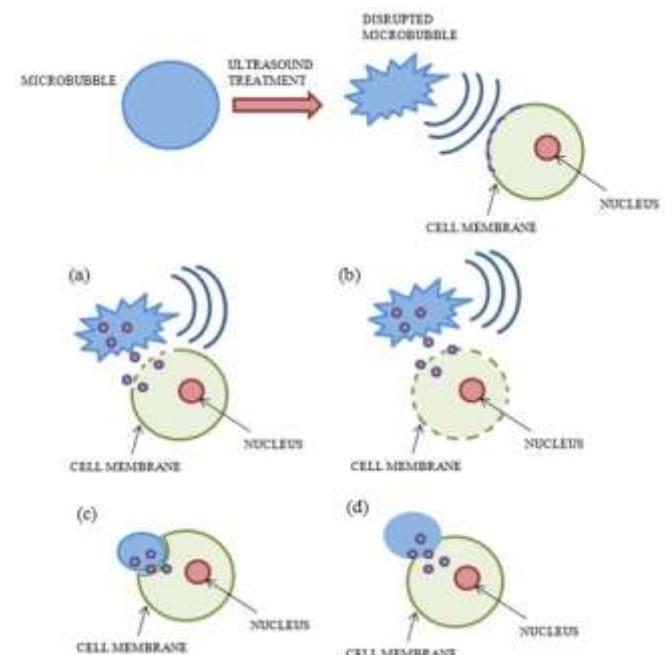
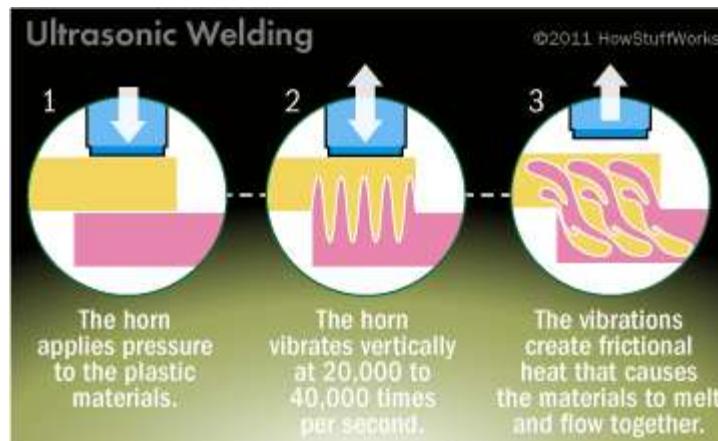
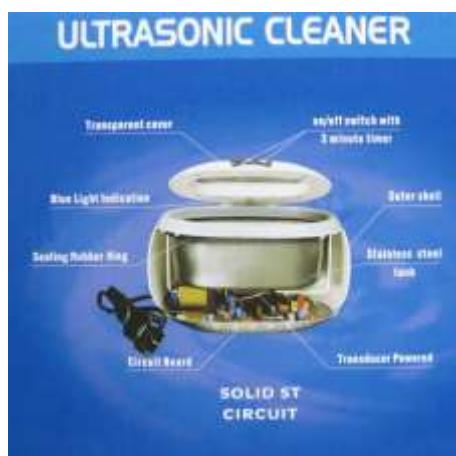
powerful  
disruption of  
phase boundary

Acoustic cavitation in liquid/liquid system

# Ultrasound

**Table 7.2 Some other uses of power ultrasound**

<i>Application</i>	<i>Examples</i>
Cleaning	Laboratory glassware; jewellery; computer components; large, delicate archaeological items
Engineering usually from 20–400 kHz	Welding and riveting of plastics, ceramic processing; drilling aid for hard, brittle materials; filtration; degassing; pigment dispersal
Biology	Disruption of cell membrane to allow extraction of contents



## **Ultrasonics/Sonochemistry – Synthesis**

### **Applications in Organic Synthesis**

#### **1. Homogeneous Sonochemistry**

- Aqueous medium
- Non-aqueous media

#### **2. Heterogeneous Sonochemistry**

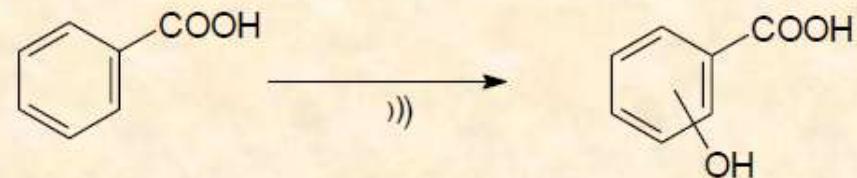
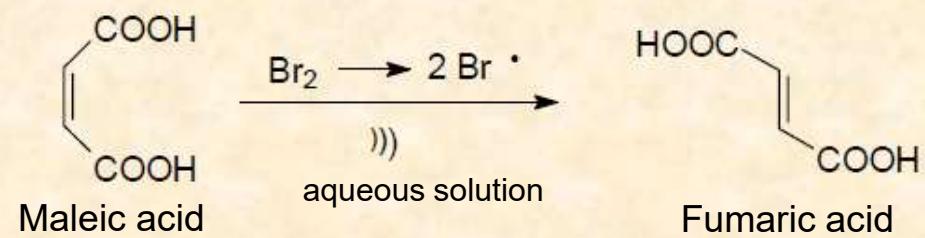
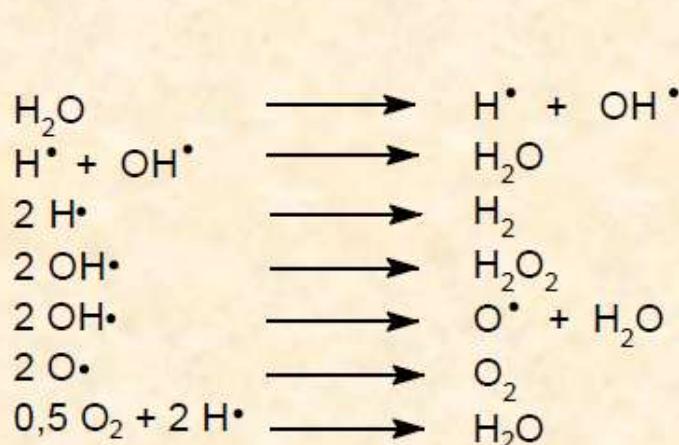
- Phase Transfer Catalysis
- Reactions with metals
- Heterogeneous Catalysis

#### **3. Enzyme reactions**

# Ultrasonics/Sonochemistry – Synthesis

## 1. Homogeneous sonochemistry

### 1.1. Aqueous sonochemistry



# Ultrasonics/Sonochemistry – Synthesis

## 1. Homogeneous sonochemistry

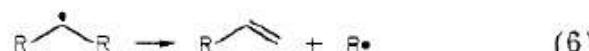
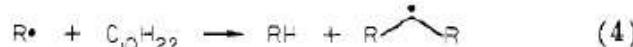
### 1.2. Non-Aqueous sonochemistry

Scheme I: Rice Radical Chain Mechanism<sup>a</sup>

initiation:



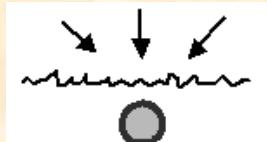
propagation:



termination:



<sup>a</sup>  $\text{R}\cdot$  = terminal radical,  $\text{R} \text{---} \overset{\bullet}{\text{C}} \text{---} \text{R}$  = internal radical.



polymer chain  
near bubble  
(not to scale)



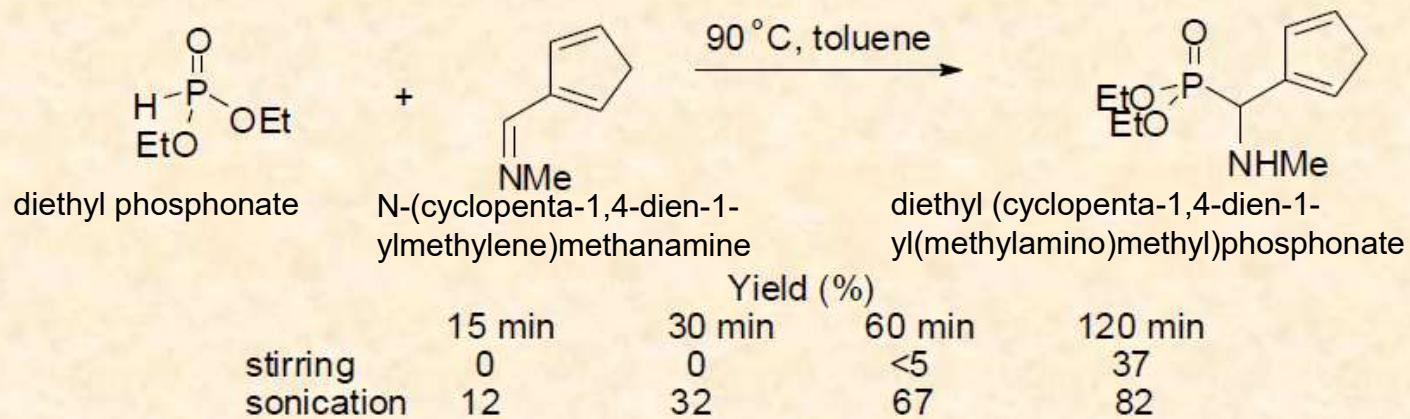
centre of chain  
becomes distorted  
due to shear forces



polymer then  
breaks into two  
macroradicals

# Ultrasonics/Sonochemistry – Synthesis

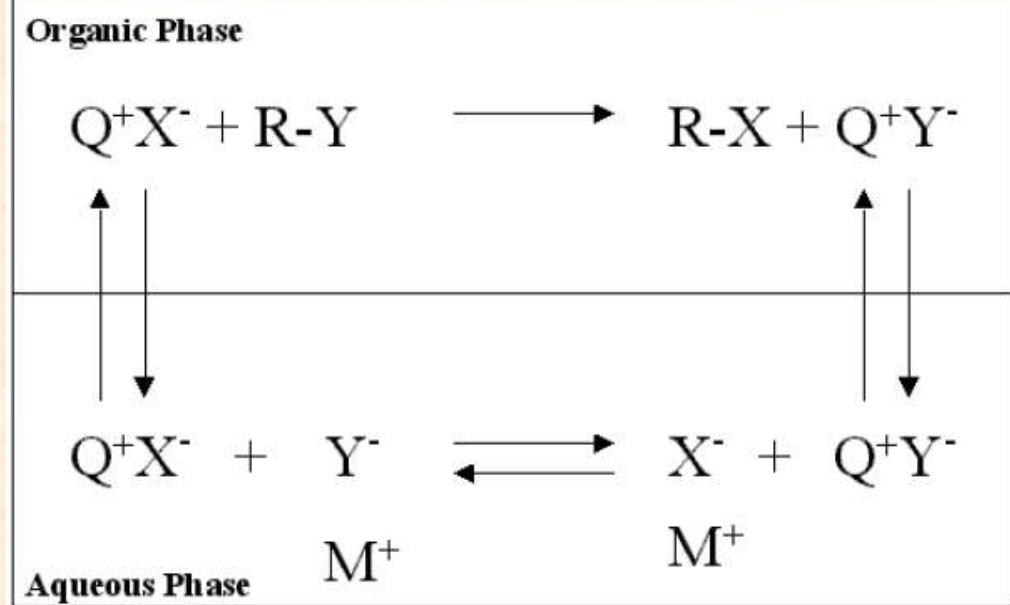
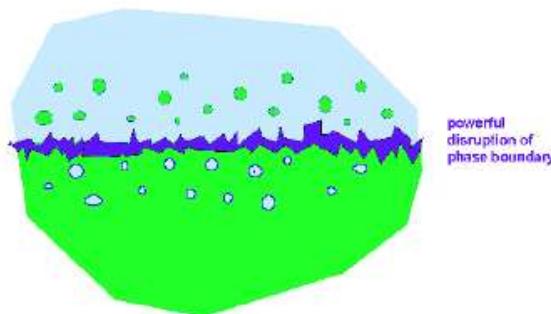
## 1.2. Non-Aqueous sonochemistry



# Ultrasonics/Sonochemistry – Synthesis

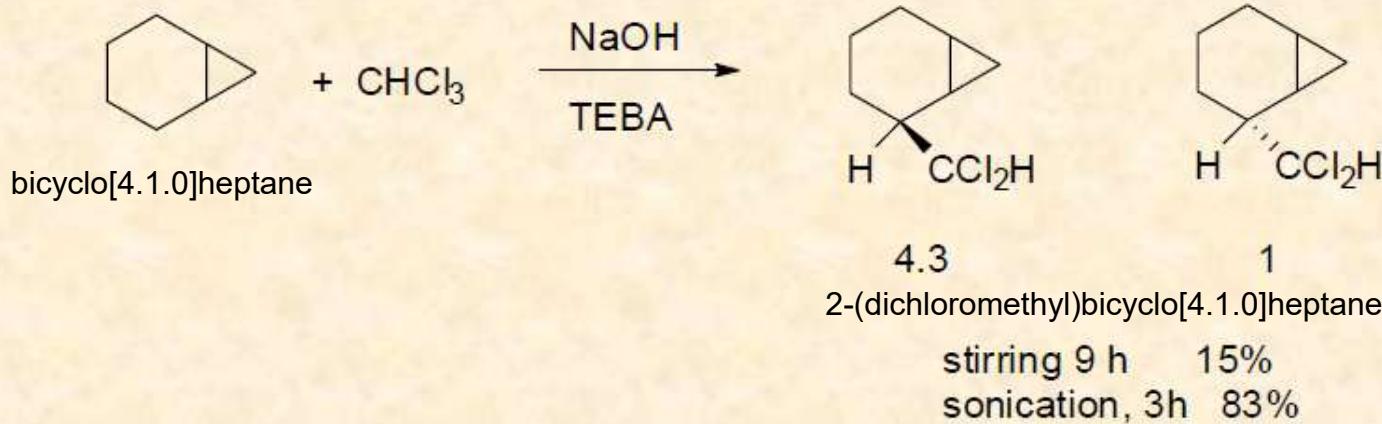
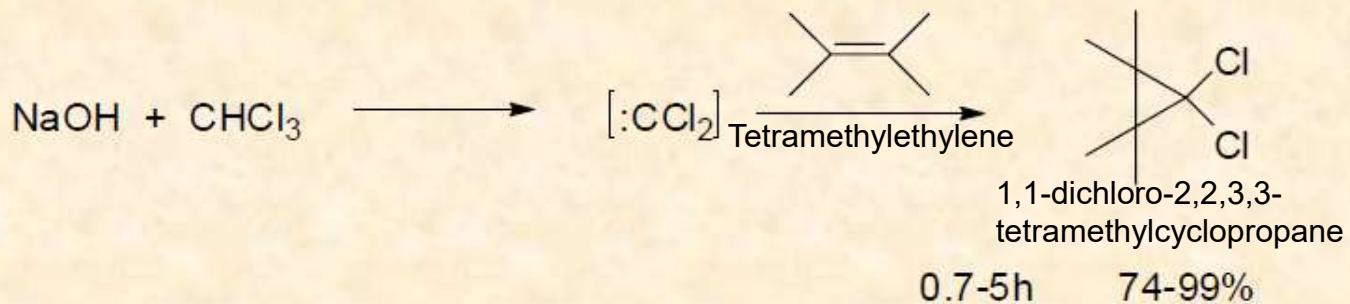
## 2. Heterogeneous sonochemistry

### 2.1. Phase transfer catalysis



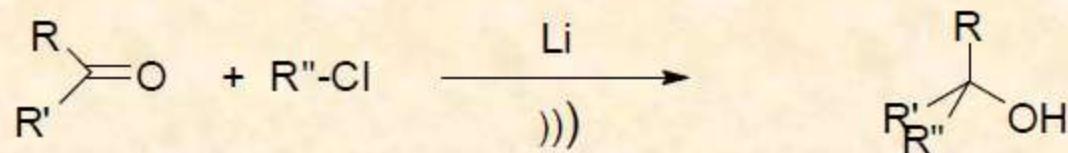
# Ultrasonics/Sonochemistry – Synthesis

## 2.1. Phase transfer catalysis

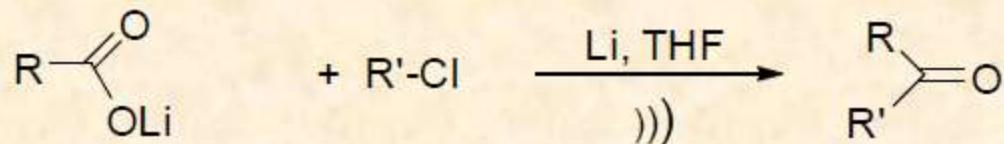


## Ultrasonics/Sonochemistry – Synthesis

### 2.2. Reactions with metals



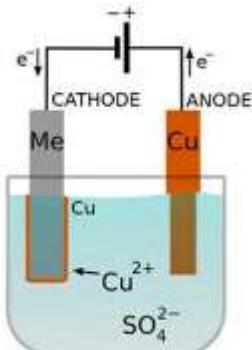
10-40 min 68-99%



72-99%

# Organic Electrochemistry

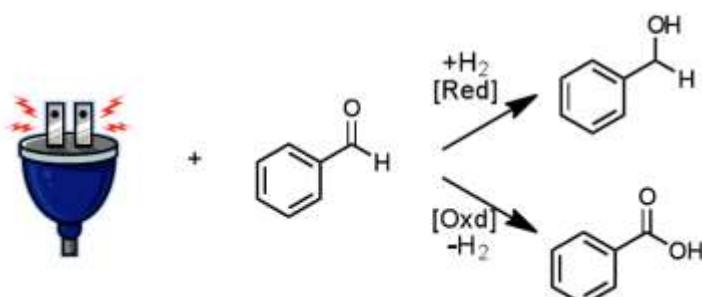
**Electrochemistry** is the branch of physical chemistry that studies the relationship between electricity and identifiable chemical change.



Electroplating

**Organic electrochemistry** is concerned with the **exchange of electrons** between a **substrate** and an **electrode** and the chemical reactions that result from such electron transfer processes.

Use of electrical current through a reaction to activate organic molecules through the addition or removal of electrons



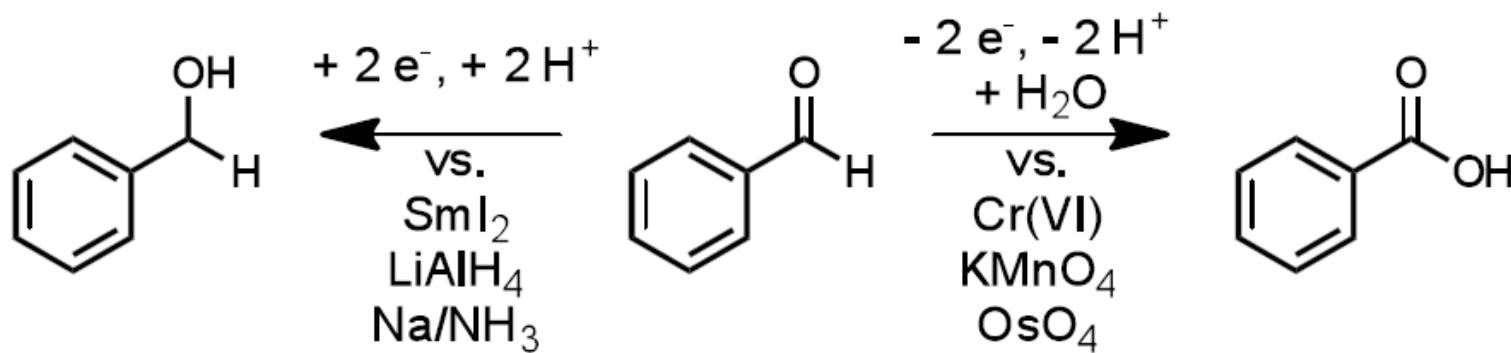
**Green benefits** of using electrochemical synthesis include

- Often **water-based processes**
- Usually **mild operating conditions** (relatively energy efficient)
- **Atom efficient** - replacement of reagents by electrons

# Organic Electrochemistry: Why?

## □ Reaction economy

- Direct control of electron energy via over potential
- Electrons/protons are (typically) sole reagents



Frontana-Uribe, B.A. et al Green Chem. 2010, 12, 2099-2119.

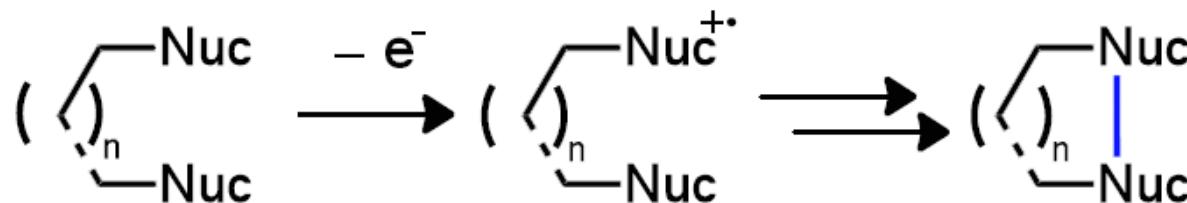
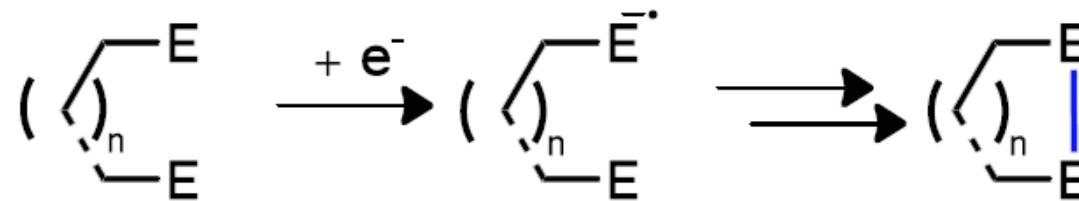
# Organic Electrochemistry: Why?

## □ Synthetic utility

- Umpolung chemistry



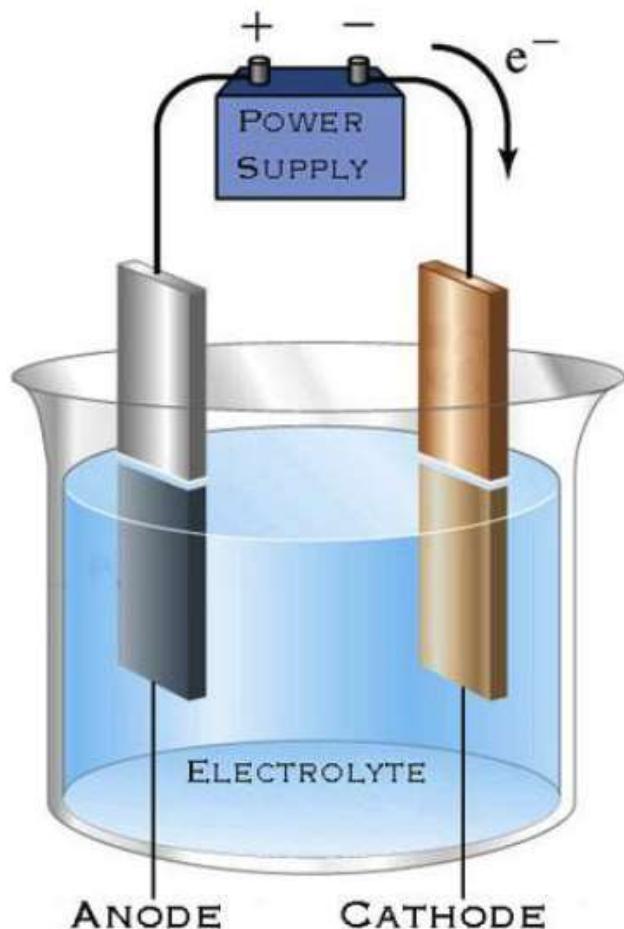
- High, typically predictable, tolerance of functional groups



$E$  = electrophile;  $Nuc$  = nucleophile

# Electrochemistry: Basics

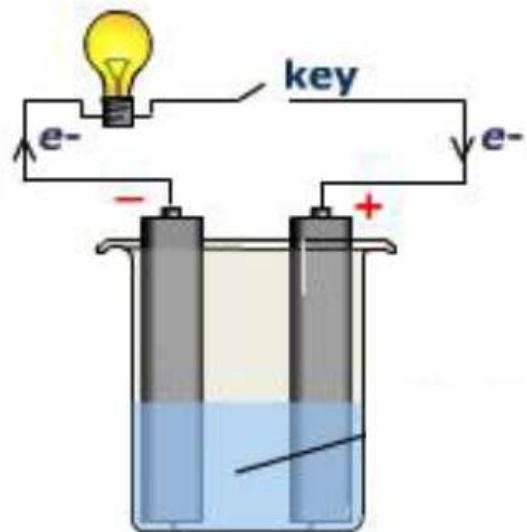
- Electrolytic cell - electricity is applied



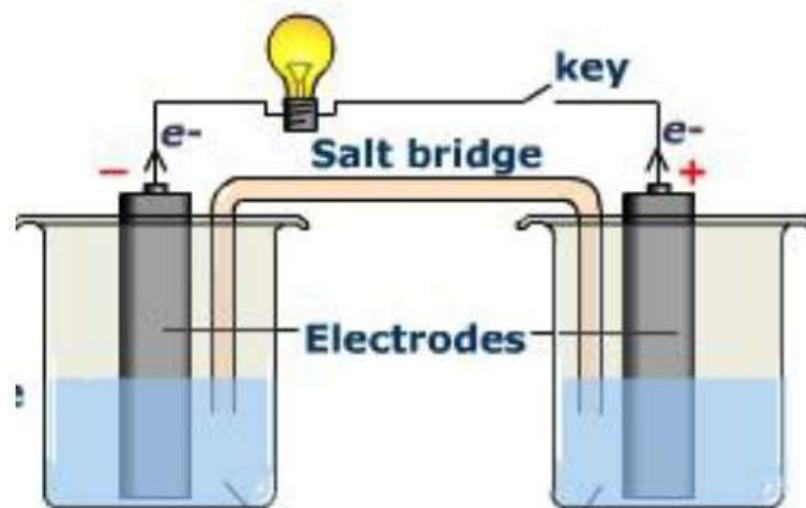
- Anode: Oxidation site
- Cathode: Reduction site
- Solvent: MeOH, CH<sub>3</sub>CN, H<sub>2</sub>O
- Electrolyte: Bu<sub>4</sub>NBF<sub>4</sub>, LiClO<sub>4</sub>, Et<sub>4</sub>NClO<sub>4</sub>
- Two methods for actions:
  - Constant current
  - Constant potential
- $\Delta G = - n F E$

# Electrochemical Cell: Design

- Two main types of cells:



Undivided



Divided

# Electrochemical Cell: Design - Undivided



- Simplest design
- Must ensure compound compatibility
- Use of protic solvents aids in reaction mediation

<http://www.gamry.com/assets/Uploads/EuroCell-Kit.jpg>

# Electrochemical Cell: Design - Divided



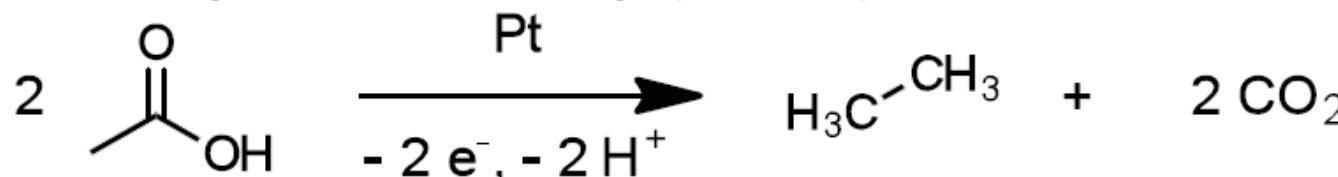
[http://www.blogs.uni-mainz.de/fb09akwaldvogel/  
files/2010/09/oximered2a2.jpg](http://www.blogs.uni-mainz.de/fb09akwaldvogel/files/2010/09/oximered2a2.jpg)

- More complex (and expensive)
- Avoids issue of compound compatibility
- Sacrificial metal or substrate in auxiliary electrode

# Organic Electrochemistry: Early Beginnings

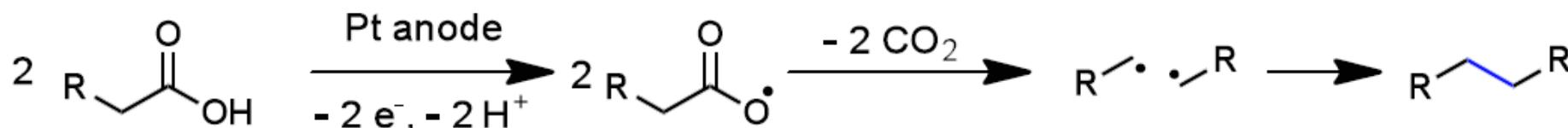
6

- 1<sup>st</sup> example – Faraday (1834):



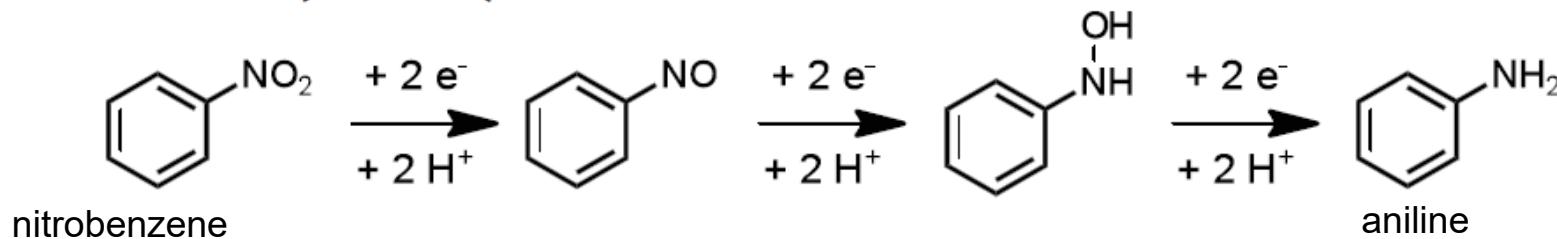
Faraday, M. Phil. Trans. R. Soc. Lond. 1834, 124, 77-122.

- Kolbe Electrolysis (1848):



Kolbe, H. Justus Liebigs Ann. Chem. 1848, 69, 257-372.

- Haber (1900):

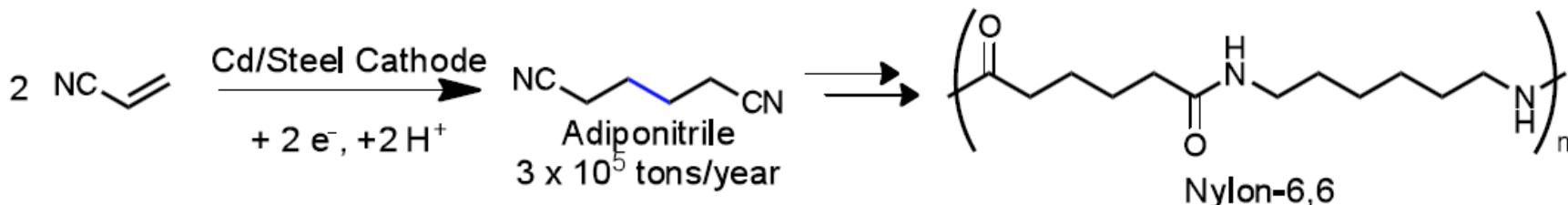


Haber, F. et al. Z.Phys. Chem. 1900, 32, 271.

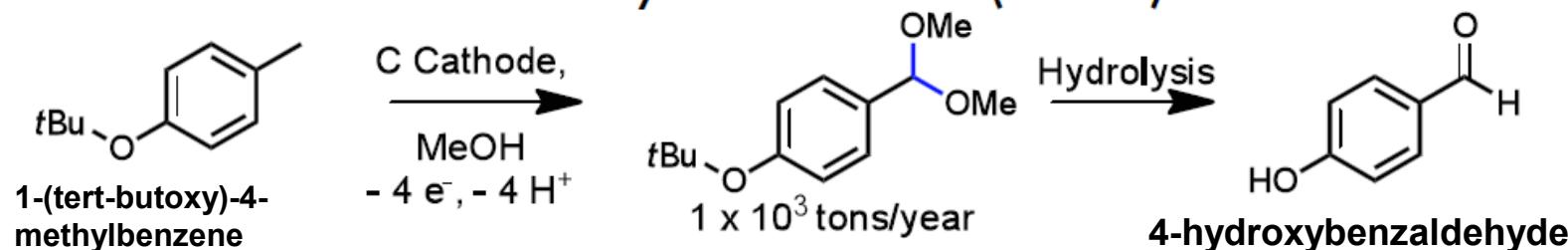
# Organic Electrochemistry: Use in industry

7

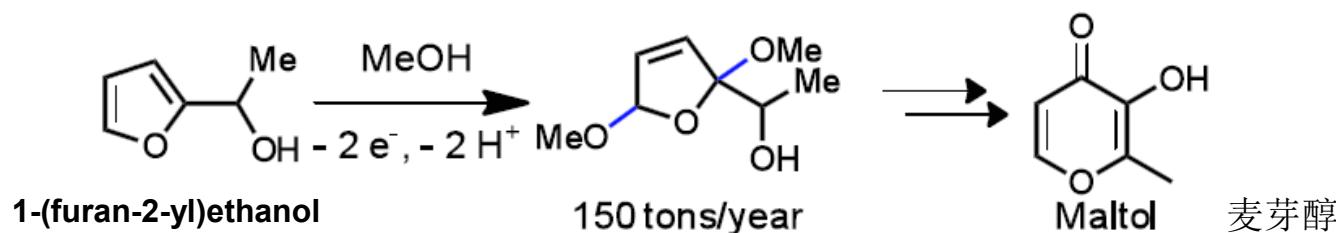
## □ Hydrodimerization of Acrylonitrile (Monsanto):



## □ Oxidation of Methyl Aromatics (BASF):

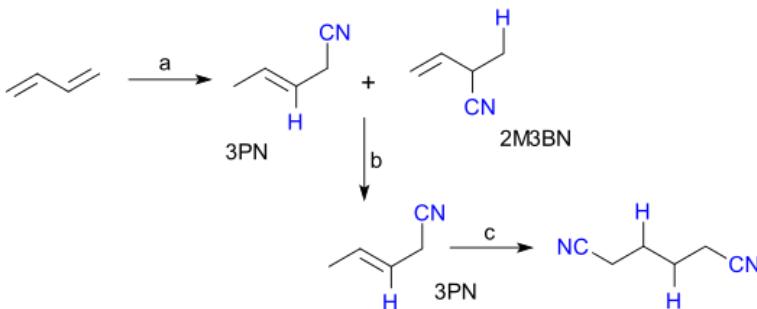


## □ Methoxylation (Otsuka):



Pletcher, D.; Walsh, F. C. Industrial Electrochemistry; Blackie Academic & Professional: Glasgow, 1993

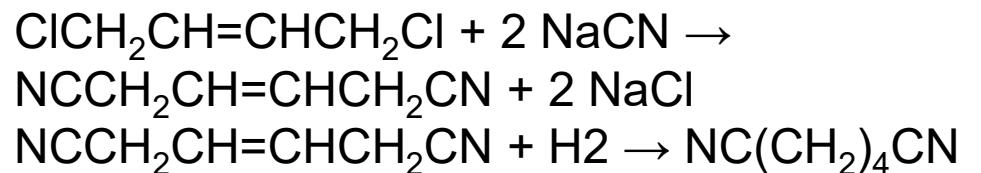
# Nickel-catalysed hydrocyanation of butadiene



- The majority of adiponitrile is prepared by the **nickel-catalysed hydrocyanation of butadiene**, as discovered at DuPont.
- The first step involves monohydrocyanation affording isomers of pentenenitriles as well as 2- and 3-methylbutenenitriles.
- In the final stage, these pentenenitriles are subjected to a second hydrocyanation to produce adiponitrile.

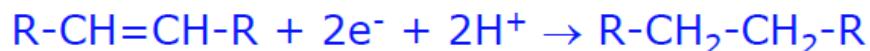
- Early industrial routes started from the **chlorination of butadiene** to give 1,4-dichloro-2-butene, which with sodium cyanide, converts to **3-hexenedinitrile**, which in turn can be hydrogenated to **adiponitrile**.

- But this process involve the applications NaCN, which is **highly toxic**, so from the consideration of green chemistry, this process is not environmentally benign.



# Reaction types

Additions:



Substitutions:



Eliminations:

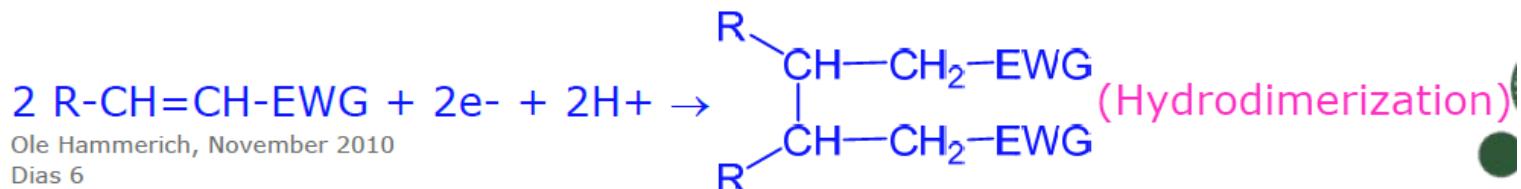


Coupling reactions:



Ole Hammerich, November 2010

Dias 6



# Conclusion

- Energy consumption, particularly for large-volume chemicals, has been taken seriously by industry for many years. Through a combination of new processes, particularly **catalytic ones, improved engineering designs** and ‘good housekeeping’, energy use continues to fall.
- The recent emergence of technologies which input energy in an alternative forms (**microwave and ultrasound**), together with renewed interest in **photochemistry and electrochemistry** for green chemistry, will lead to selected future processes being more energy efficient as well as cleaner.

# Presentation

- Oct. 12:胡晨斌,陆嘉宁,沙新虎
- Oct. 19:侯天新,顾千禧,尹笑一
- Oct. 26:施婉婷,杨晨愉,周敬艺
- Nov. 02:王鹏,华辰,吴梓欣
- Nov. 09:马祥云,刘冀,贺承莹
- Nov.16:张玲,陈玉洁,陈华炜
- Nov.23:李新宇,杨心儿,王亦陈
- Nov. 30:孔旭恬,陈彦妤,严逸舟
- Dec. 07:曹宇航,仇嘉浩,王永泉
- Dec. 14:李云昊,陈韵轩,周路广
- Dec. 21:周颂颂,孙瑞鸽,温雅
- Dec.28:周小棠,梅艳