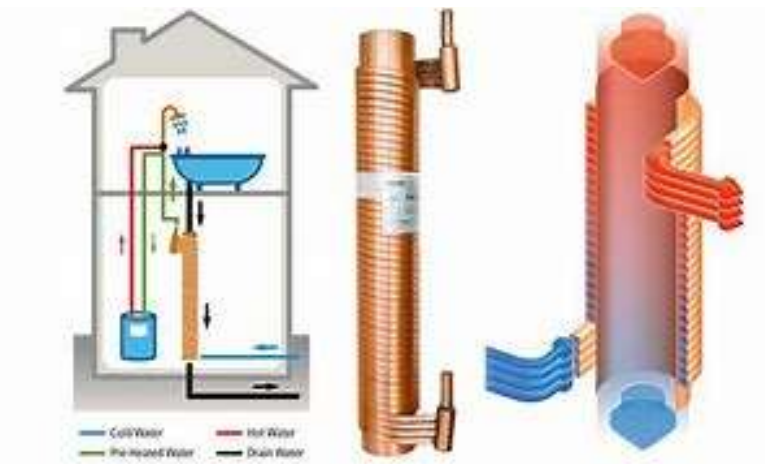




Xinming Li  
College of Chemistry, Chemical Engineering  
and Material Science  
Email: [xinmingli@suda.edu.cn](mailto:xinmingli@suda.edu.cn)  
Office: 912-0607

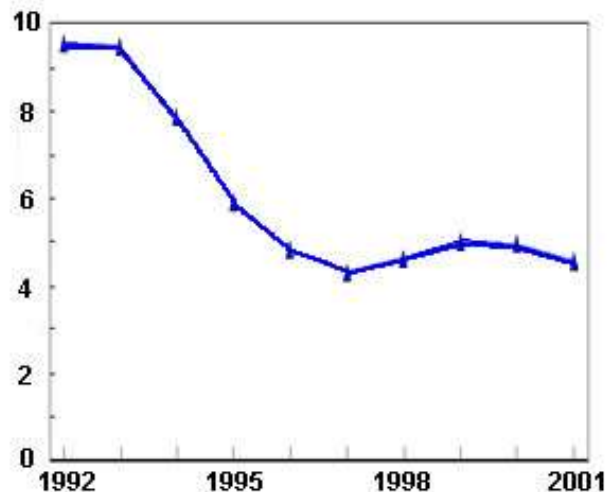


Solar power

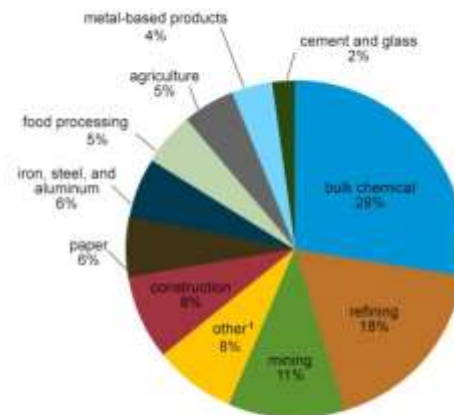
**Monitoring, control and maintenance**  
**Loss prevention**  
**Waste heat recovery**  
**Matching energy sources to requirements**

# Highly efficient synthetic techniques to achieve green process

Energy consumption  
(GigaJoules per tonne of product)



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 (6%).  
Source: U.S. Energy Information Administration, *Annual Energy Outlook 2018*, Tables 25-35, February 2018.



## Microwave Ovens

Cooking Food!



Household MW ovens

Cooking Chemistry ???



The Use of Microwave Ovens for Rapid Organic Synthesis R. Gedye et al., *Tetrahedron Lett.* 1986, 27, 279.

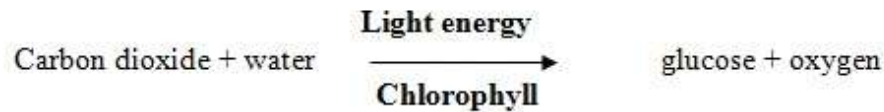


# Highly efficient synthetic techniques to achieve green process

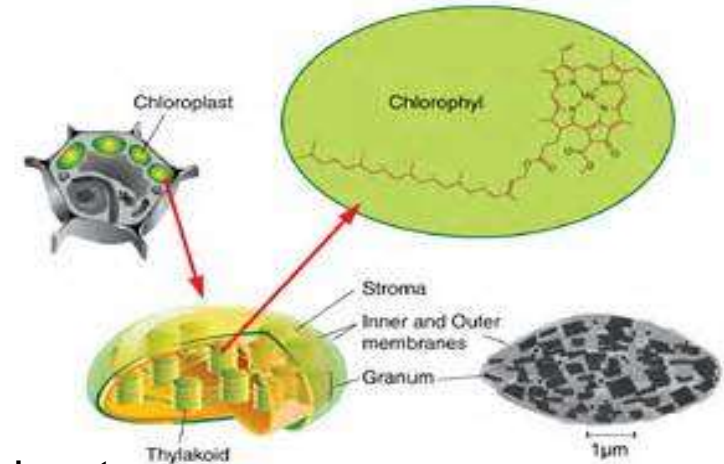
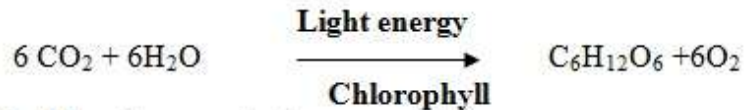
- Photochemical reactions
- Chemistry with microwaves
- Sonochemistry (ultrasound in synthetic chemistry)
- Electrochemical synthesis

# Photochemical reaction in nature

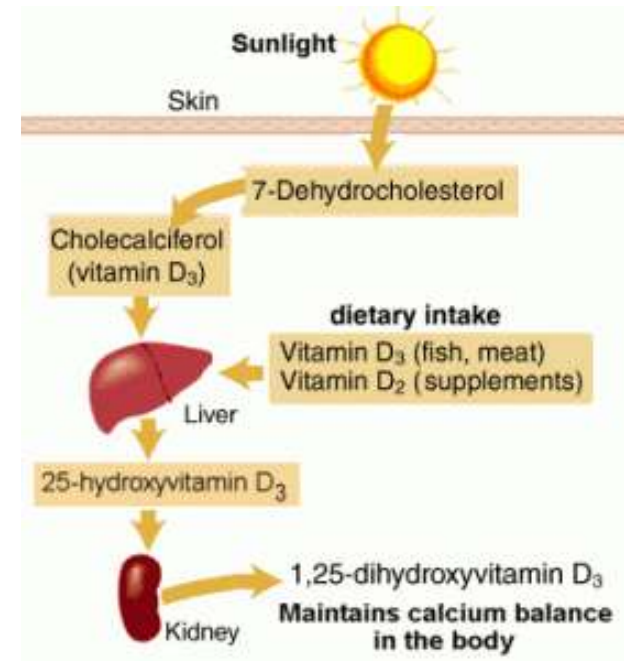
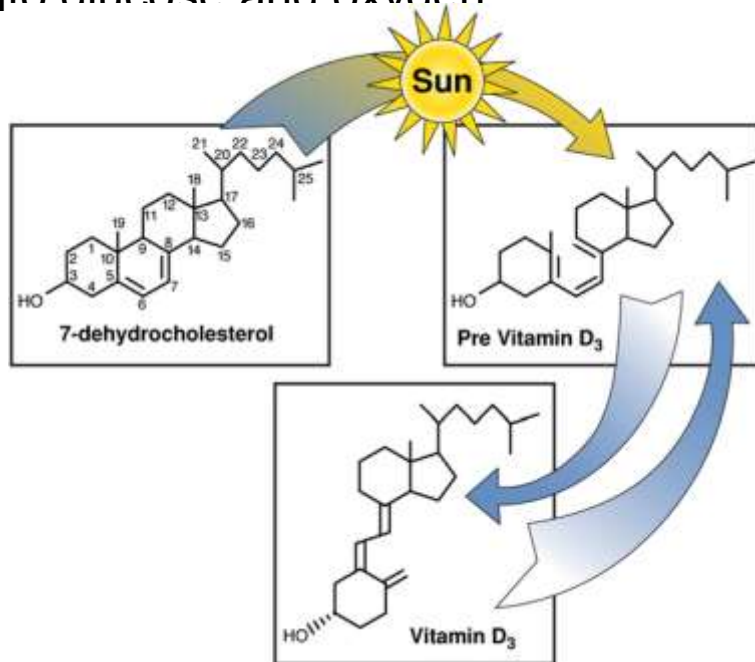
## Photosynthesis:



### Balanced equation



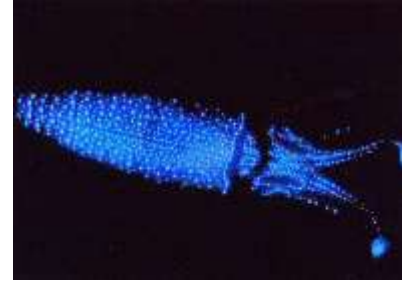
Plants use solar energy to convert carbon dioxide and water into glucose and oxygen



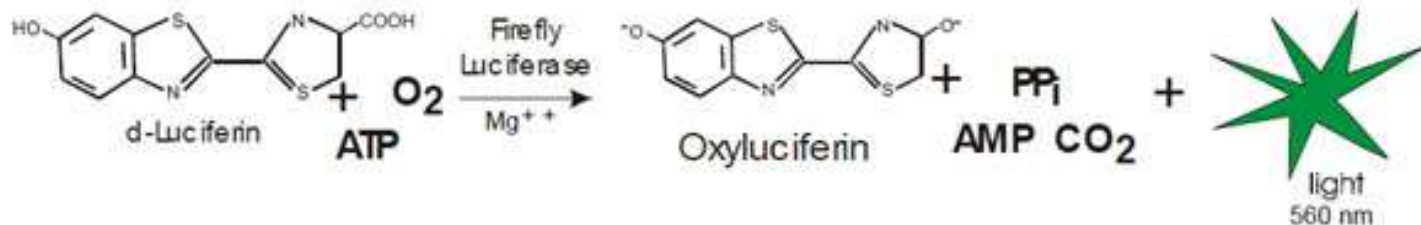
Formation of vitamin D<sub>3</sub> by exposure to sunlight in nature.

# Photochemical reaction in nature

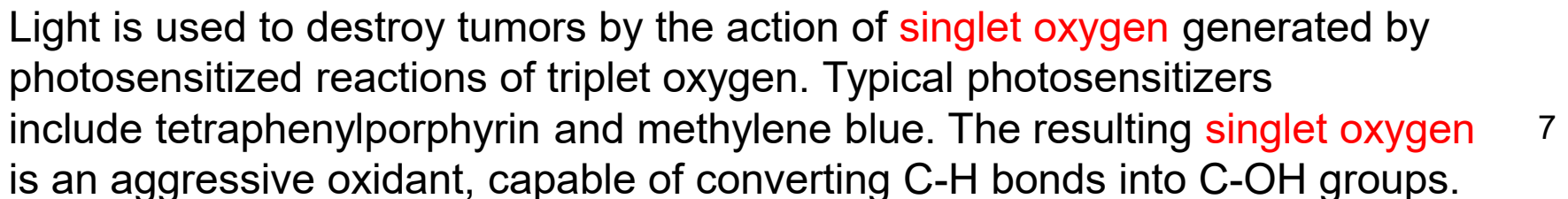
## Bioluminescence:



- 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.**

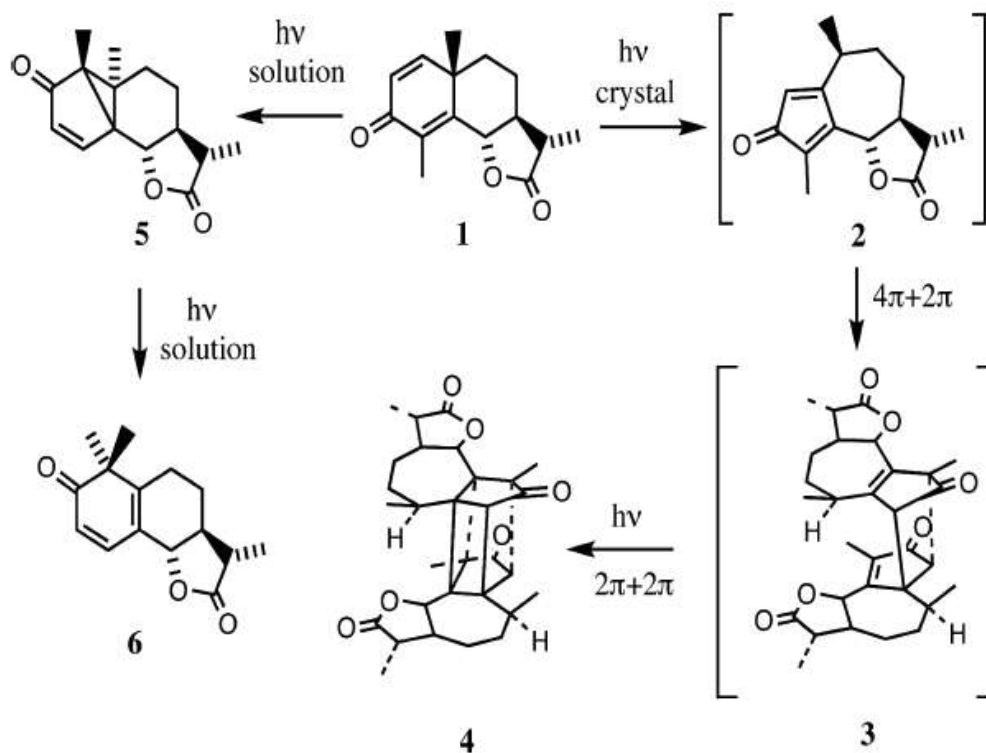


# Photocarcinogenesis



# The Beginnings of Organic Photochemistry

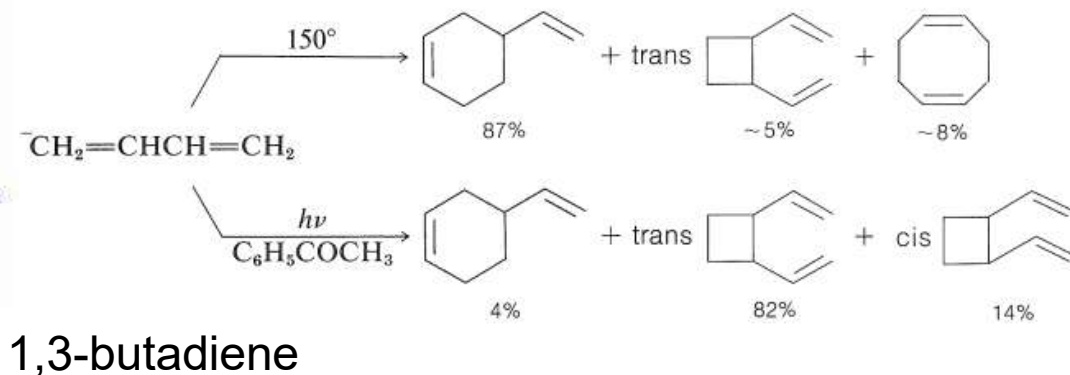
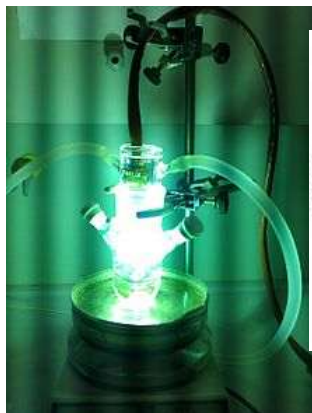
**1834:** First photochemical transformation described by Trommsdorff: Exposed  $\alpha$ -Santonin (**1**) crystals to sunlight and observed that they turned yellow and bursted. The mechanism was elucidated in 2007 by Arunkumar Natarajan et al.



山道年

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

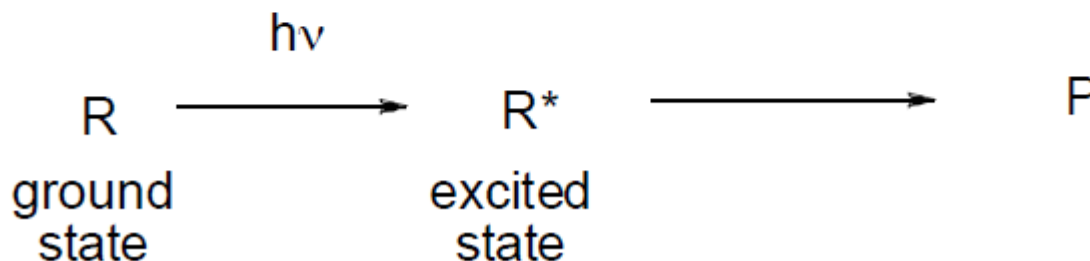


- **Photochemical reaction**, a chemical reaction initiated by the absorption of energy in the form of **light**.
- The consequence of molecules' absorbing light is the creation of **transient excited states** whose chemical and physical properties differ greatly from the original molecules.
- Photochemical 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.”*

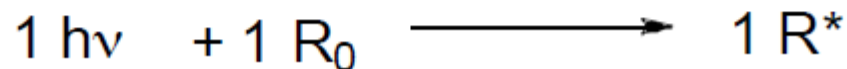


**Grotthus–Draper law:** Light must be absorbed by a chemical substance in order for a photochemical reaction to take place.

# 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

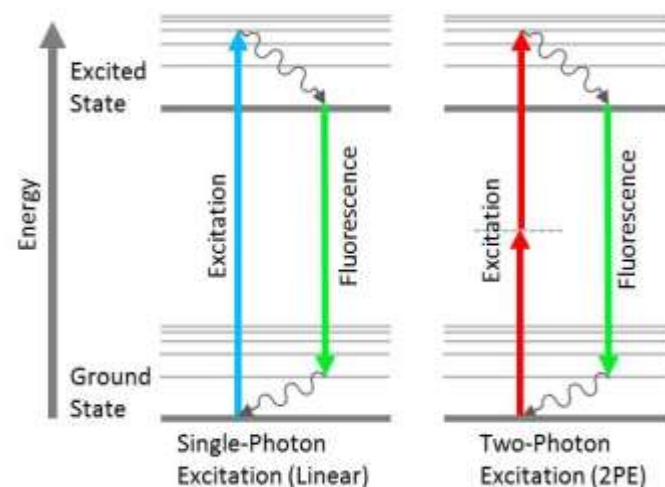
$E_0$  = energy of ground state

$h$  = 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

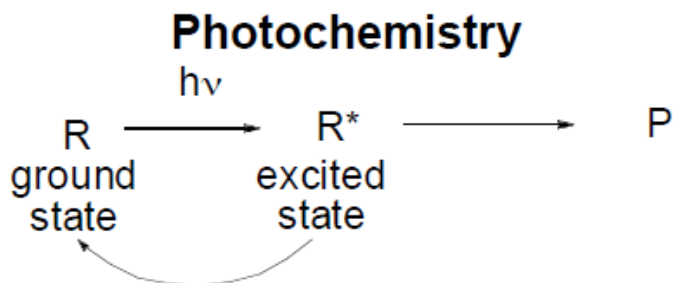
Electronic transitions involves a shift of one electrons from a lower to a higher energy molecular orbital. In most cases these molecular orbitals are associated with a specific part (e.g. functional group) of the molecule. *This part, that mainly absorbs the photon is termed the **chromophore**.*

Examples are aryl units, polyenes, and other pi-bonds, carbonyl, -NO<sub>2</sub>, -N<sub>3</sub> 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	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCH}_3 \end{array}$	<i>n</i> -Hexane	186 280	1,000 16	$n \rightarrow \sigma^*$ $n \rightarrow \pi^*$
	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH} \end{array}$	<i>n</i> -Hexane	180 293	Large 12	$n \rightarrow \sigma^*$ $n \rightarrow \pi^*$
Carboxyl	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{COH} \end{array}$	Ethanol	204	41	$n \rightarrow \pi^*$
Amido	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CNH}_2 \end{array}$	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	$n \rightarrow \pi^*$

Dr. Samer HOUSHEH



**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

### 2) Decay Processes

*-Return to ground state with release of energy*

Quenching – energy transfer

Fluorescence

Phosphorescence

Luminescence

## Photochemical Processes

*- Chemical reactions of the excited state*

fragmentations

cis/trans isomerizations

rearrangements

addition/cyclization reactions

photo oxidations

### *Important Compound Classes*

alkenes, dienes & polyenes

aromatic compounds

carbonyl compounds

nitrogen-containing compounds

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

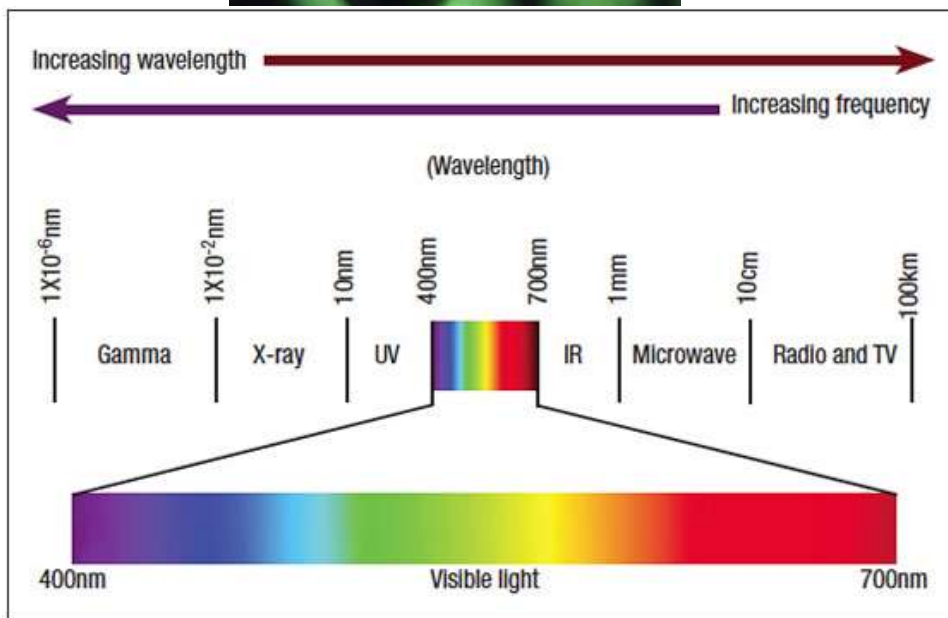
singlet oxygen

halogen-containing compounds

# Experimental set-up

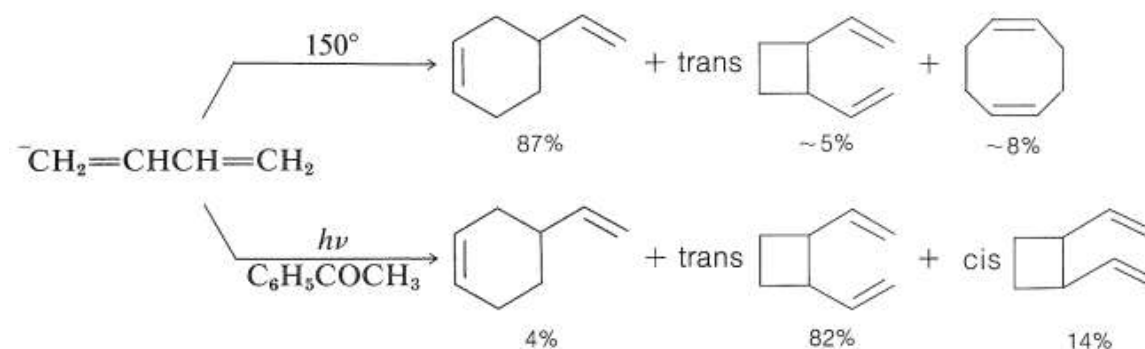


- A light source that emits wavelengths corresponding to an **electronic transition in the reactant**.
- Reactors: **Quartz** is used for the reactors as well as to contain the **lamp**. **Normal glassware** absorbs at wavelengths shorter than **275 nm**.
- Solvents: Different solvents can **absorb photons**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

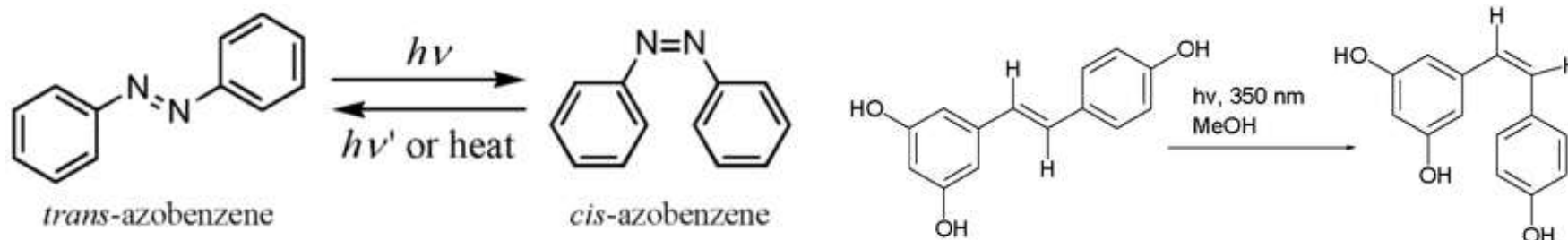


# Advantages of and Challenges Faced by Photochemical Processes

- **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.**



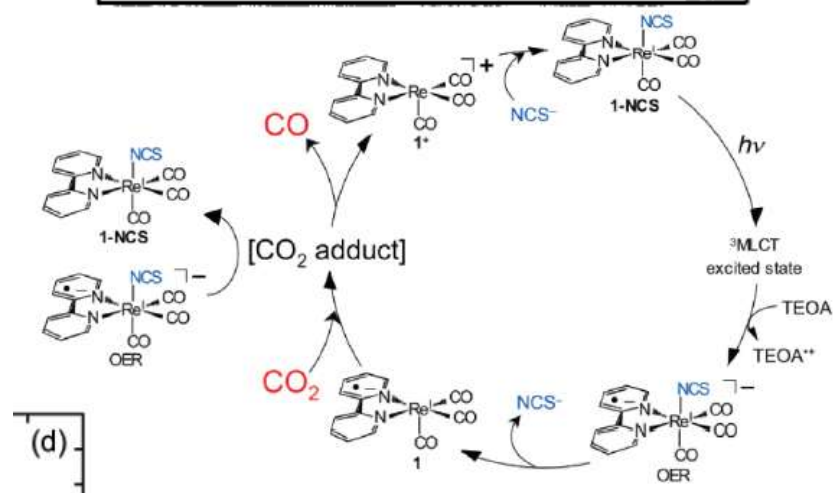
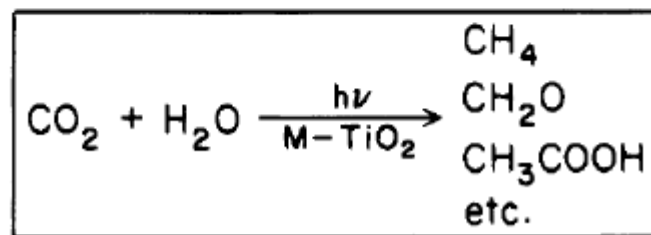
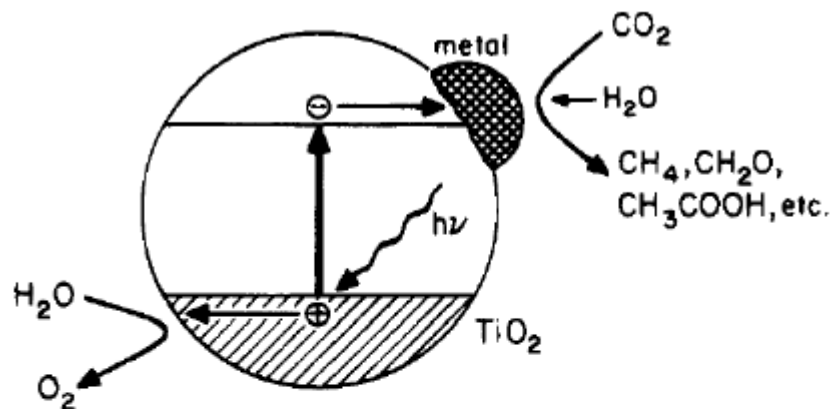
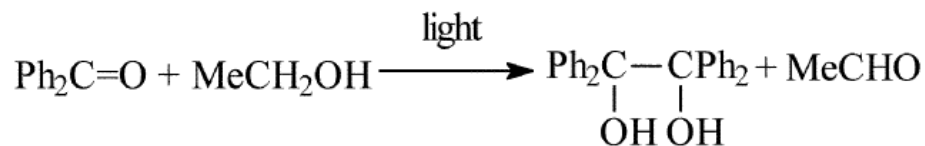
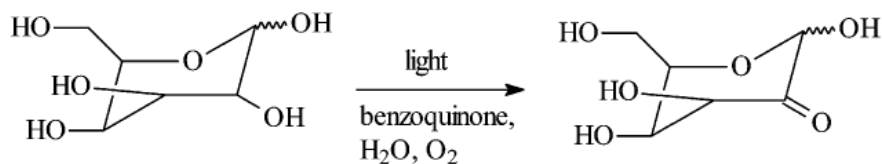
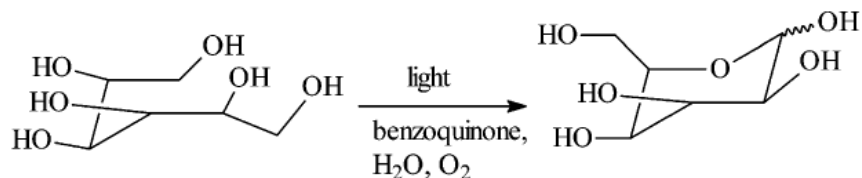
# Photoisomerization reaction



- **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**.

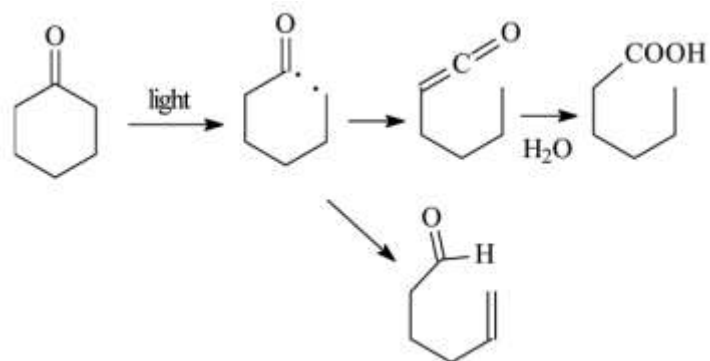
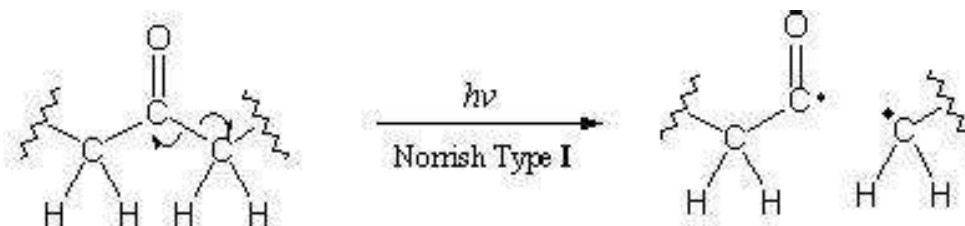


Green Chem., 2004, 6, 1–6

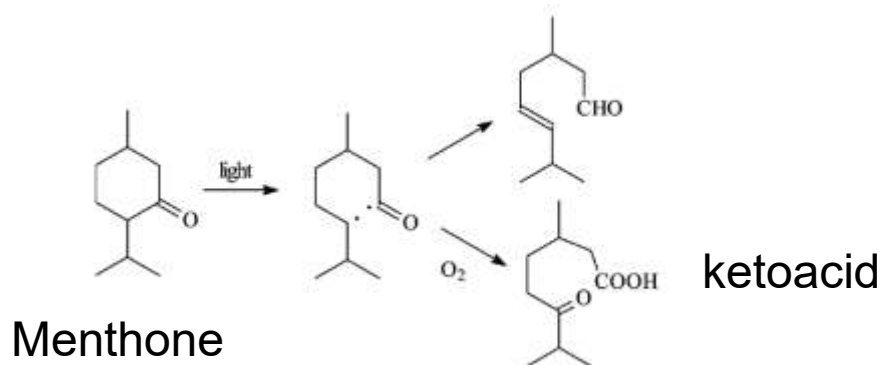
Journal of the American Chemical Society **2008**, 130, 2023-2031.

# Fragmentation reaction

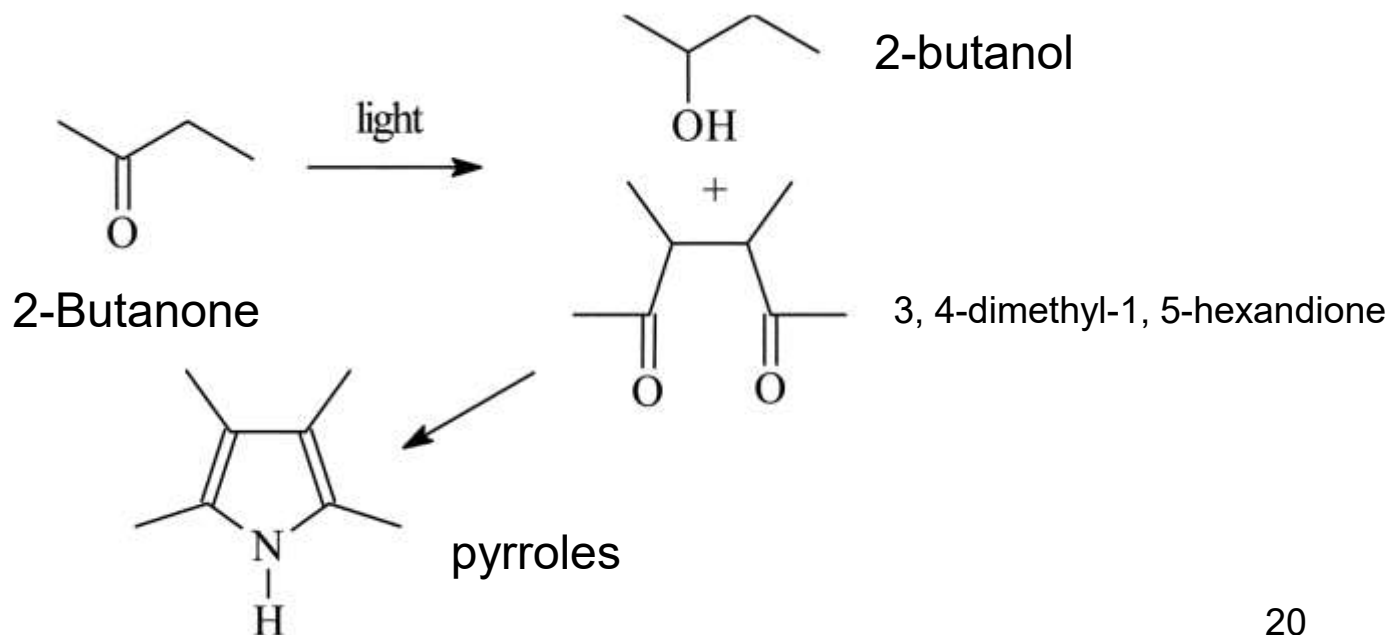
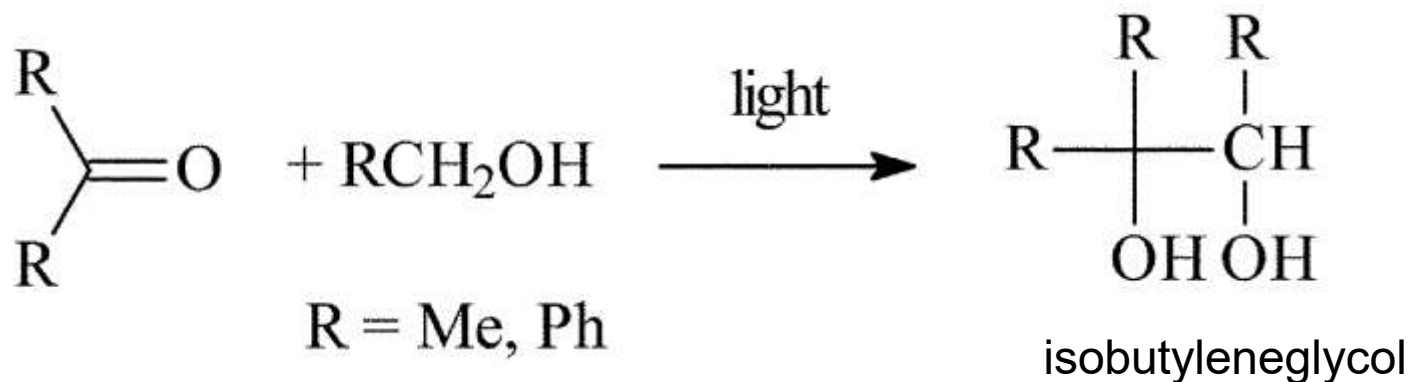
Norrish I Type reaction



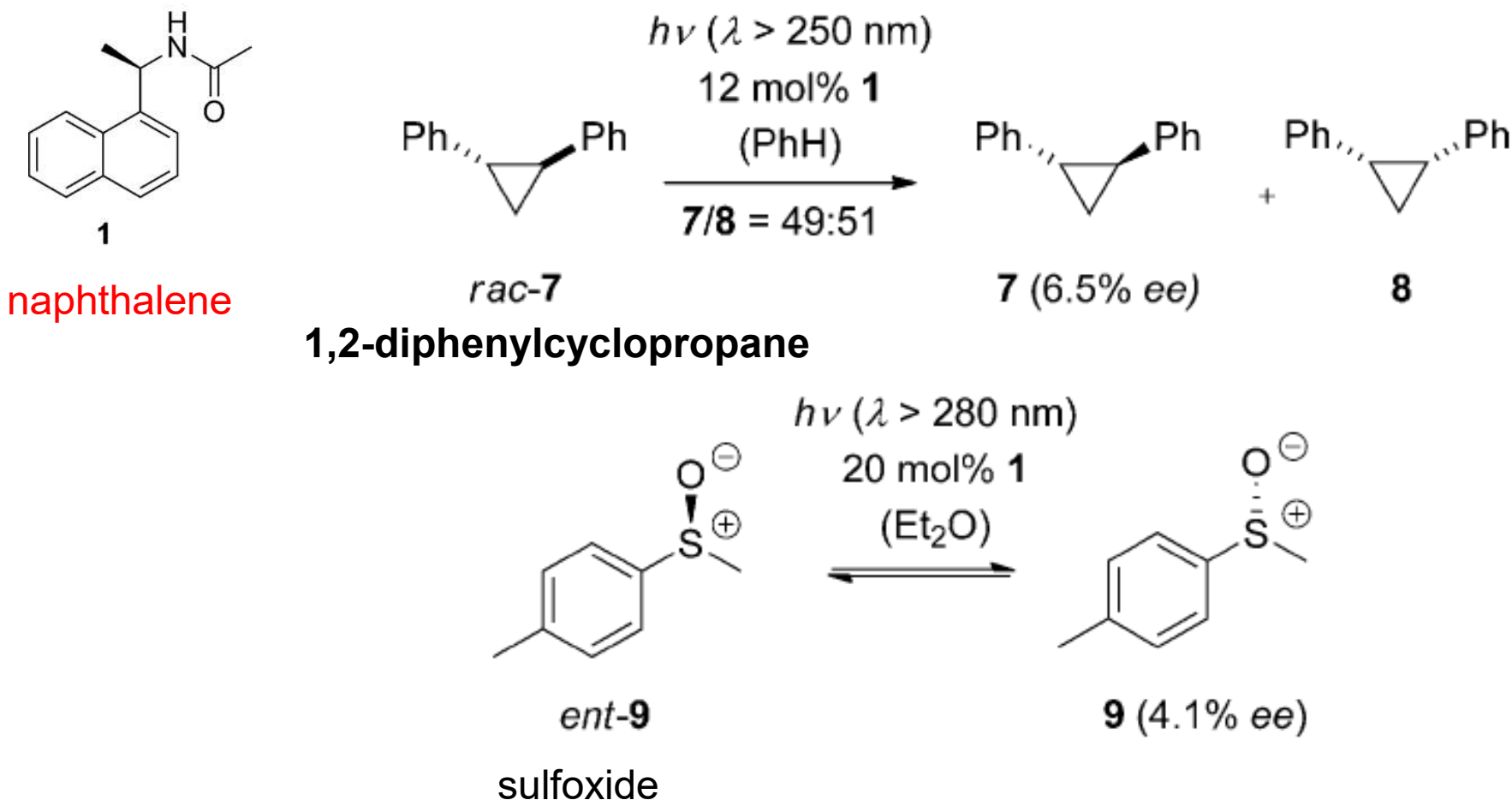
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# Condensation reactions

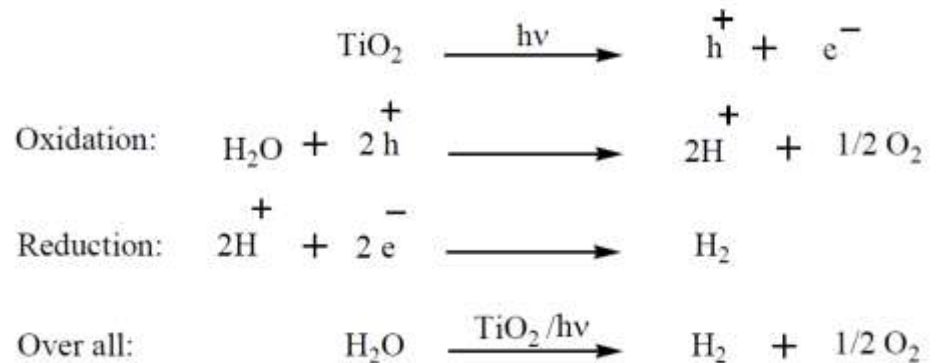
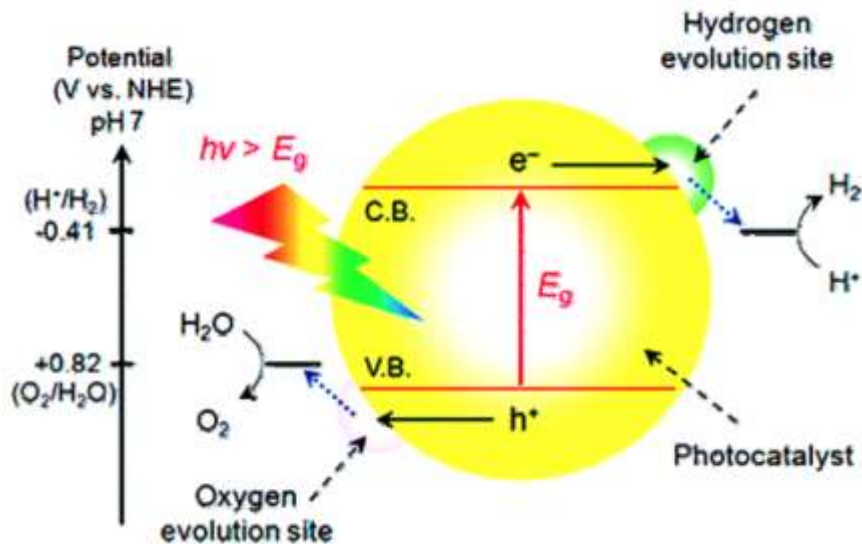


# Enantioselective Reactions

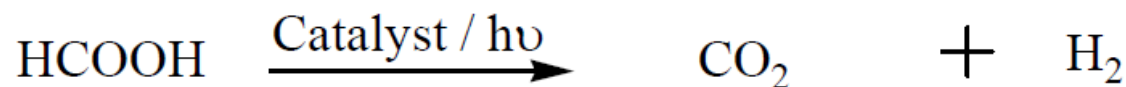
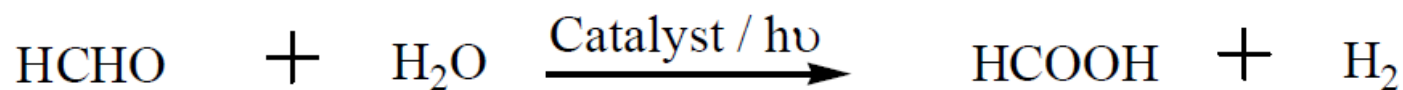
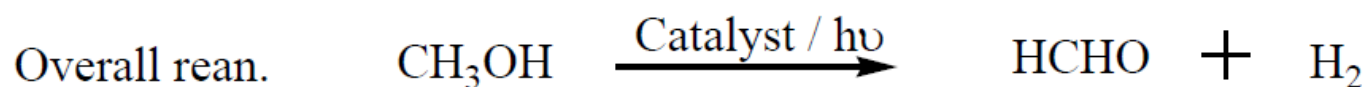
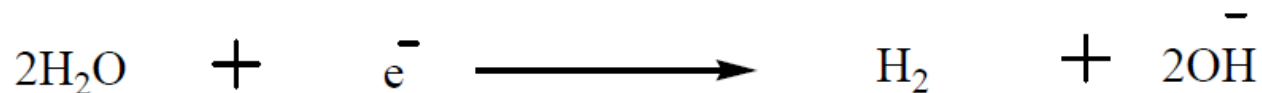
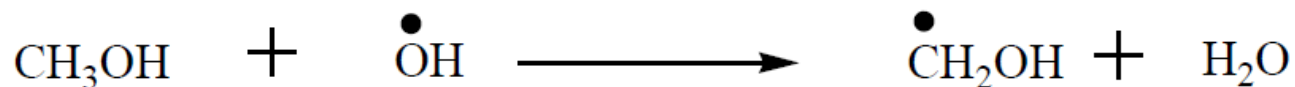
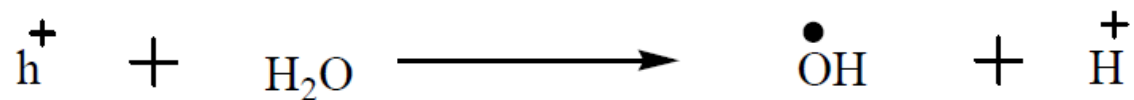


# photocatalyst

- 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.



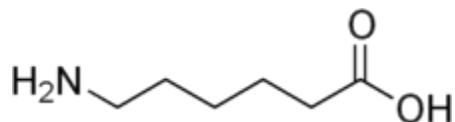
## Photocatalytic Water Splitting Reaction



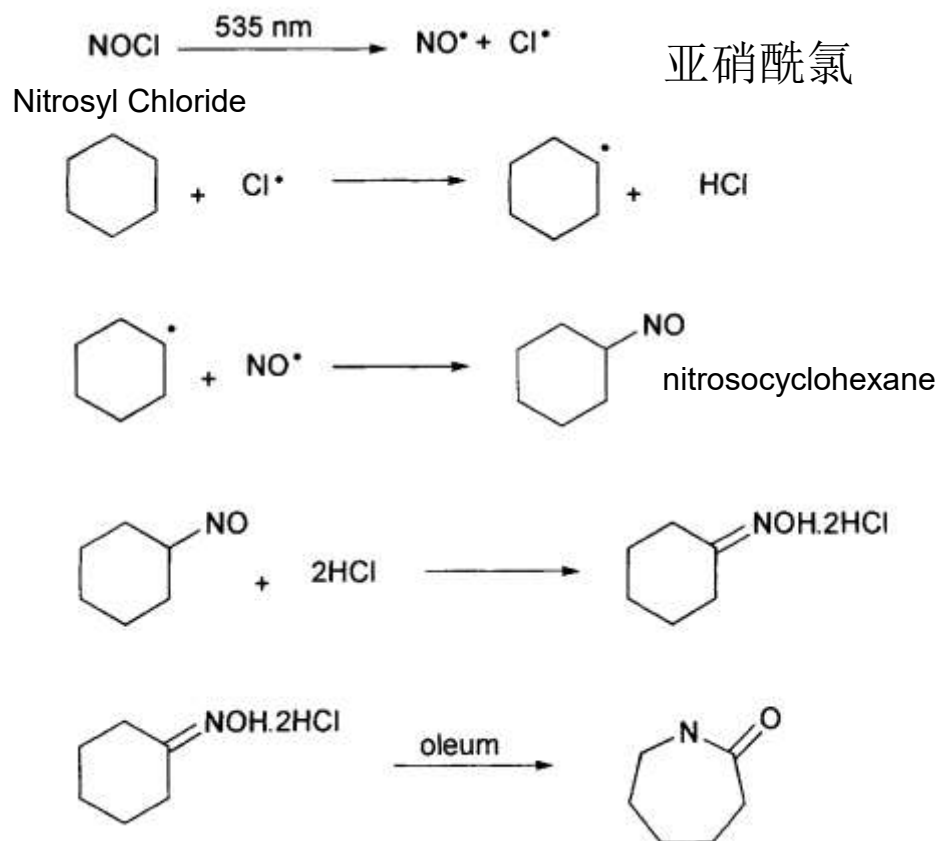
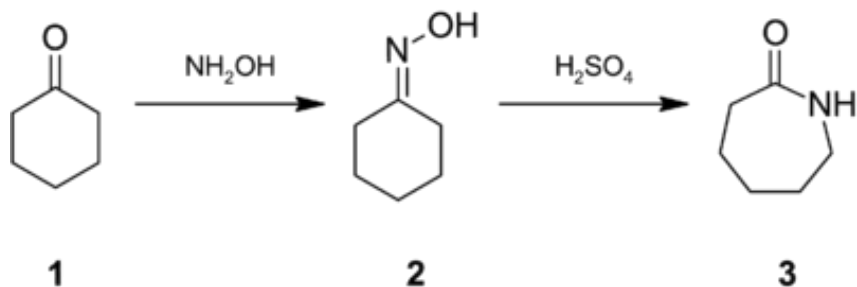
# Examples of Photochemical Reactions

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

Conventional method



$\epsilon$ -aminocaproic acid

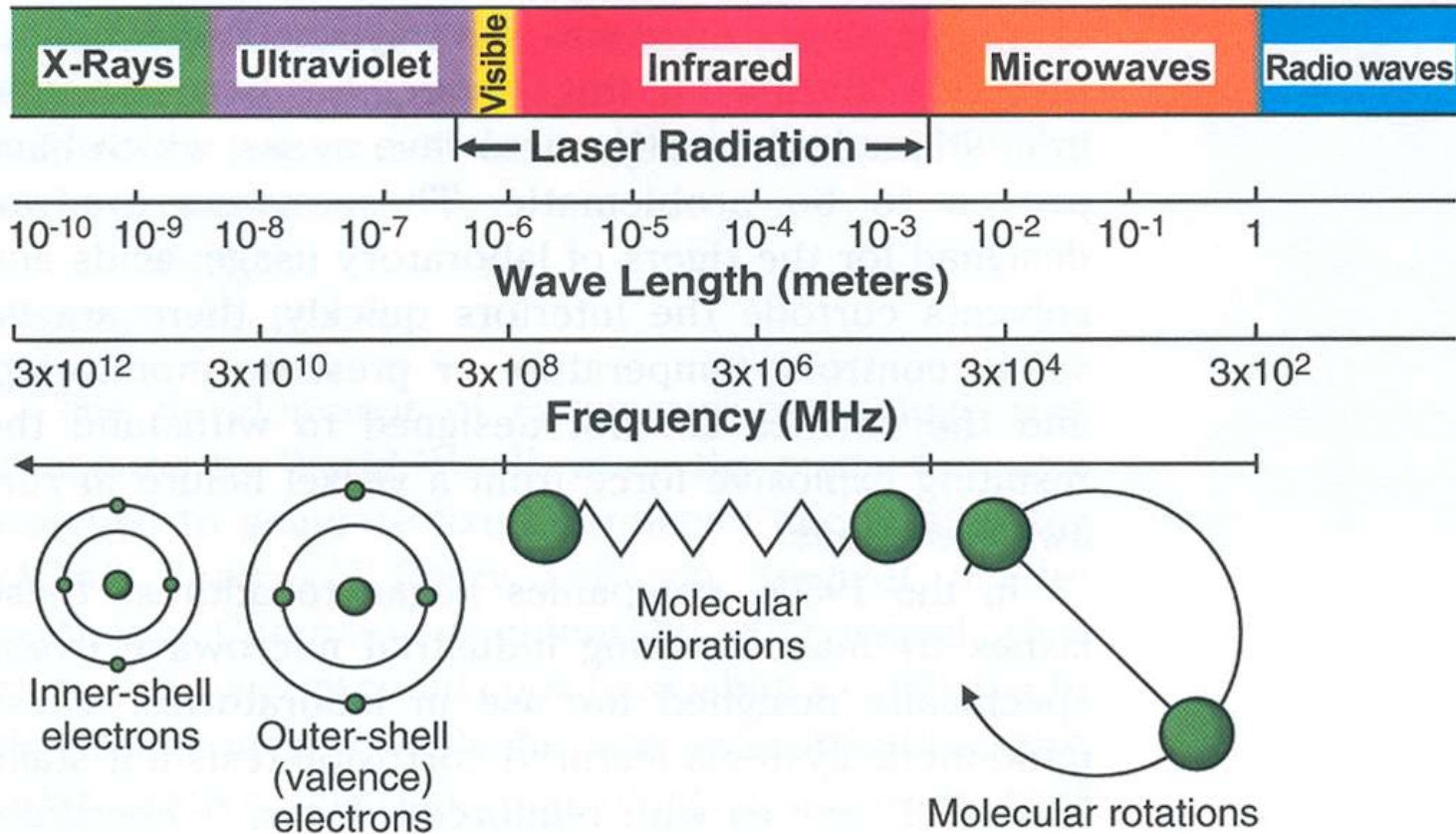


# Challenges Faced by Photochemical Processes

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

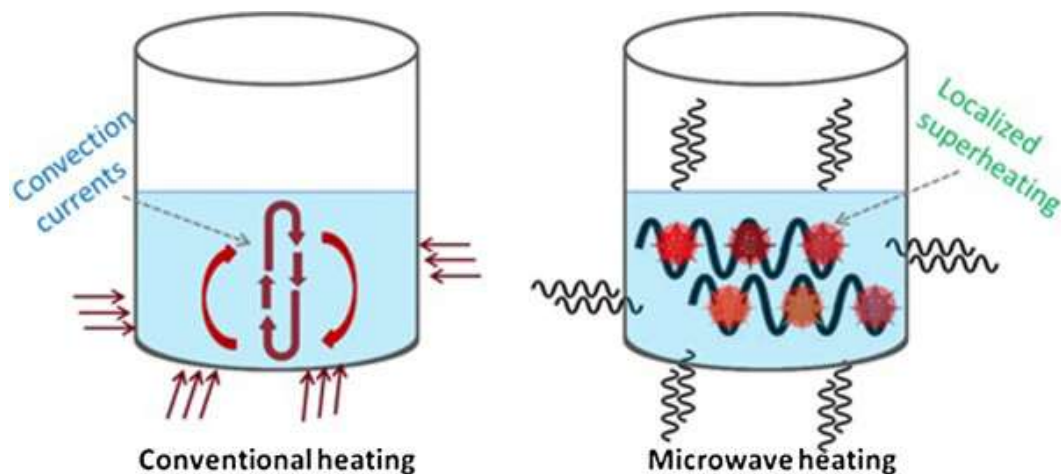
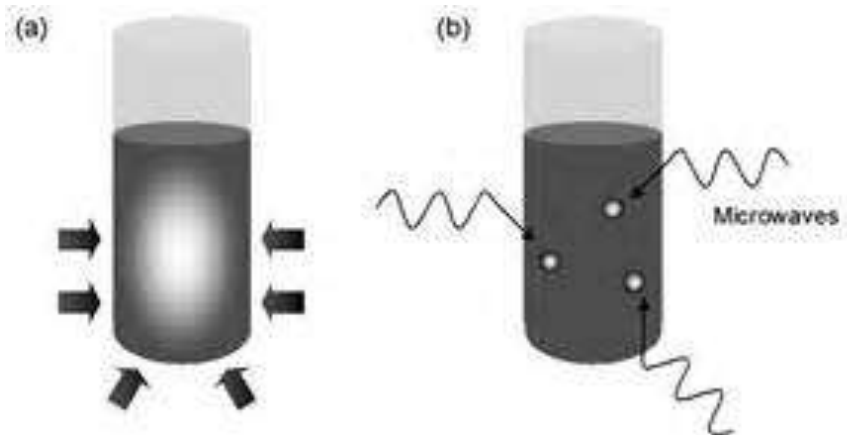
# Microwaves

*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**.

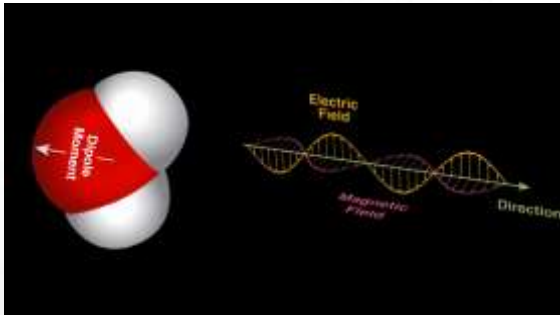
# Chemistry with microwaves



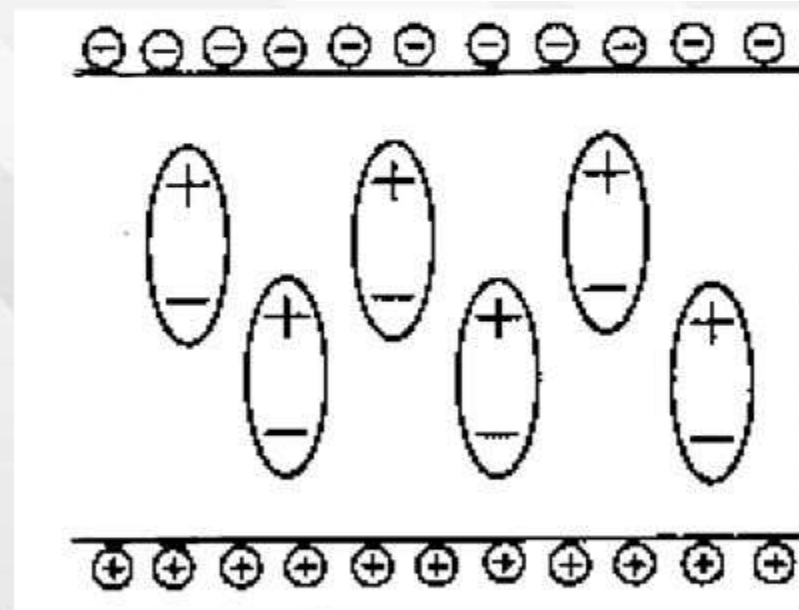
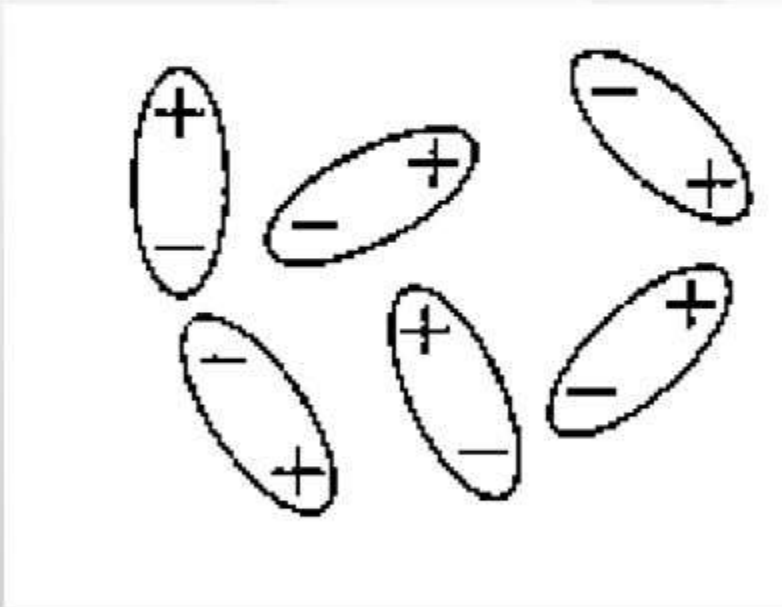
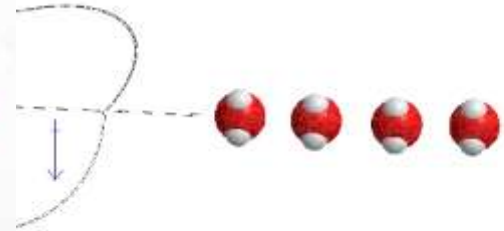
- Microwaves may be considered a more **efficient source of heating** than conventional **steam- or oil heated vessels** since the energy is **directly** imparted to the **reaction medium** rather than through the walls of a reaction vessel.

# Mechanism of Microwave Heating

www.warlock.com.au



## Dipole Rotation



Microwave heating occurs when the molecules become polarized by an alternating electromagnetic field. Rapid rotational movement of the molecules inside the materials cause collisions with neighboring molecules. The ensuing result 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**.

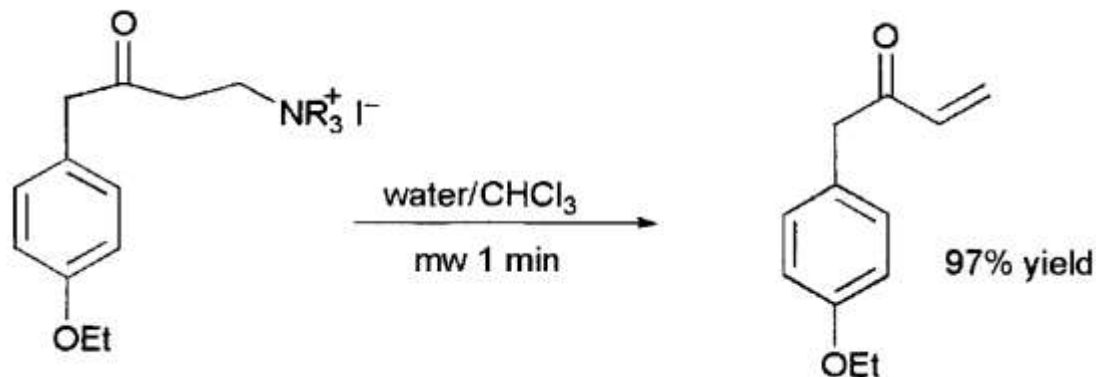
Challenges: The natural limitations on solvents imposed by microwave heating, has led to many reactions being carried out in **water** or, more commonly, under **solvent-free conditions**.

- 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

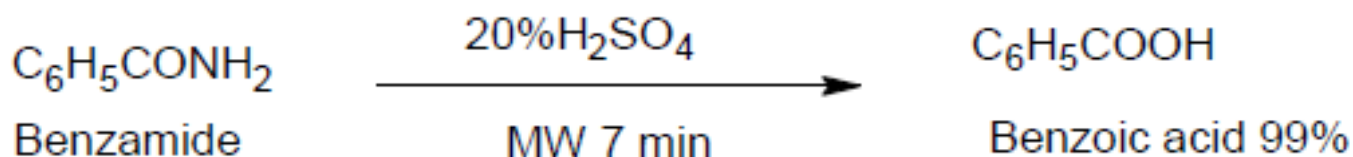
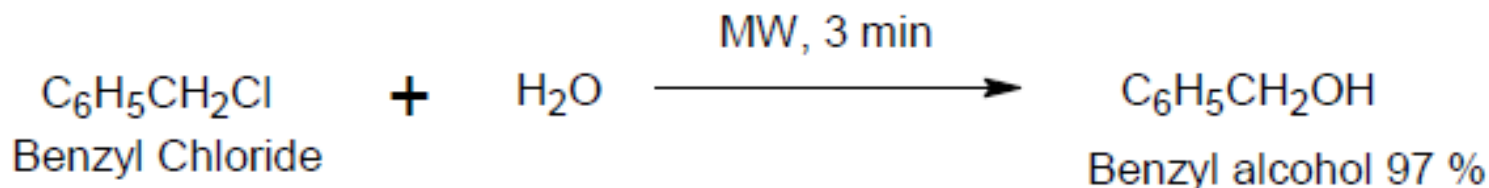


4-amino-1- 4-methoxyphenyl butan-2-one

- 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

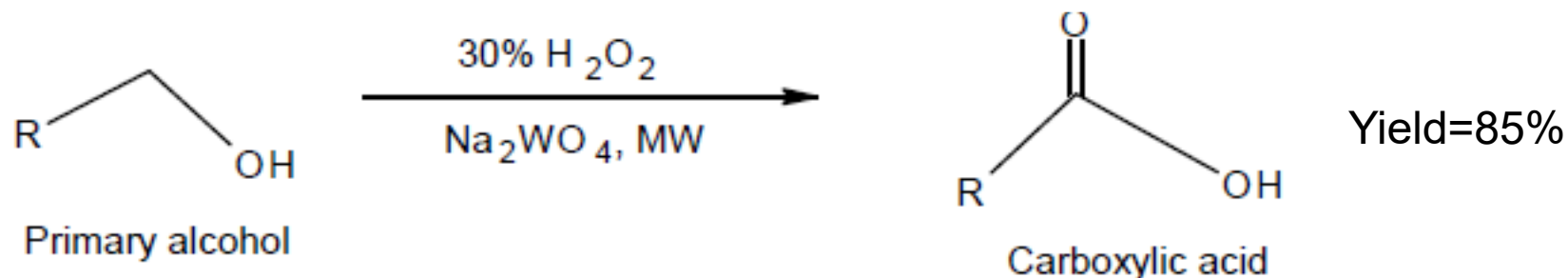


Quantitative conversion was achieved in **7 min** under microwave irradiation at **140 °C**, compared to a 90% conversion after a 1-h **reflux** using a conventional heating source.

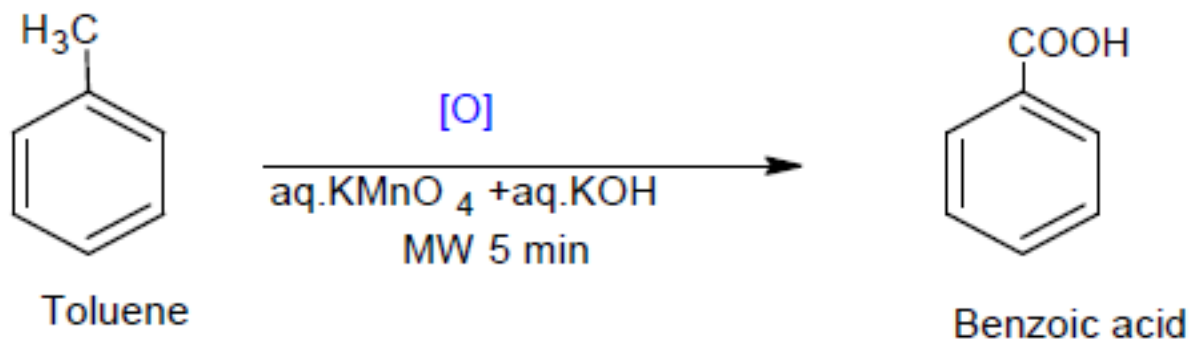
The difference in reaction time can be accounted for by **the difference in reaction temperature** coupled **with the very rapid heating of the microwave reactor**.

# Microwave Assisted Reactions

## Oxidation

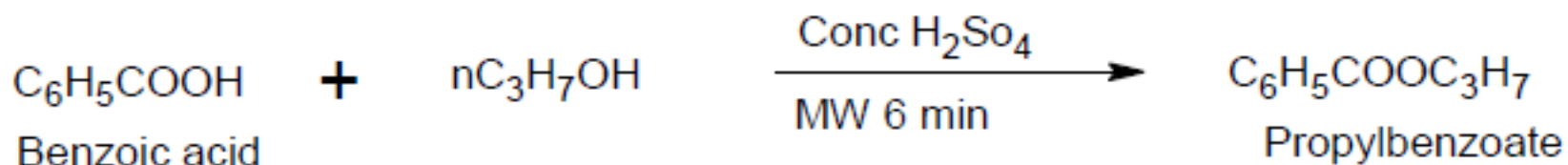


A range of primary alcohols have been oxidized to the corresponding carboxylic acids using sodium tungstate as catalyst in 30% aqueous hydrogen peroxide.



# Microwave Assisted Reactions

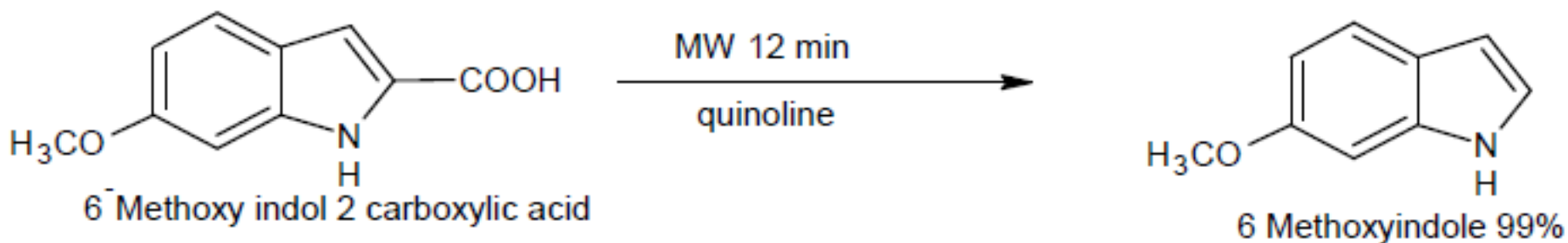
## Esterification



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

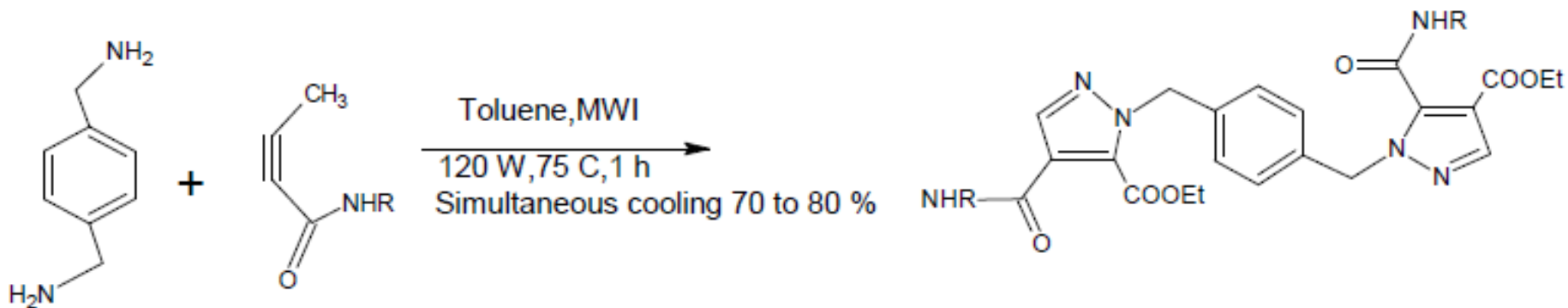
## Decarboxylation



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

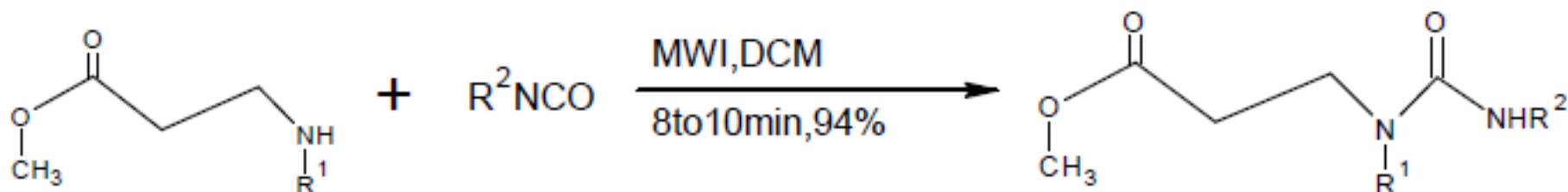
## Cycloaddition



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

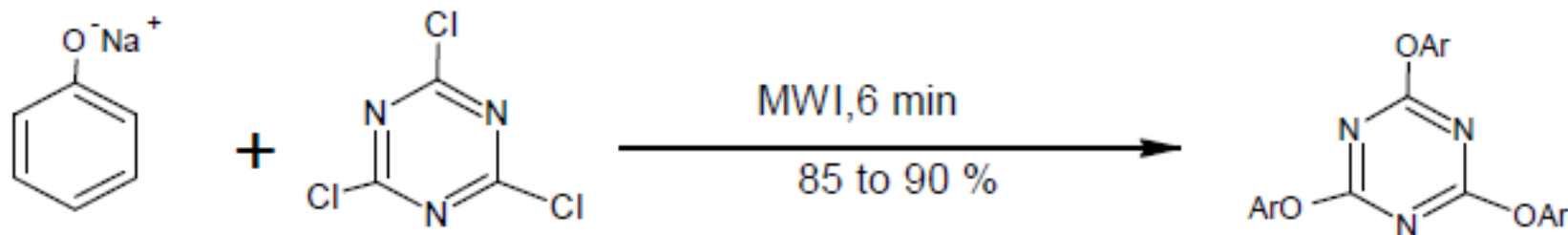
## N-Acylations



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

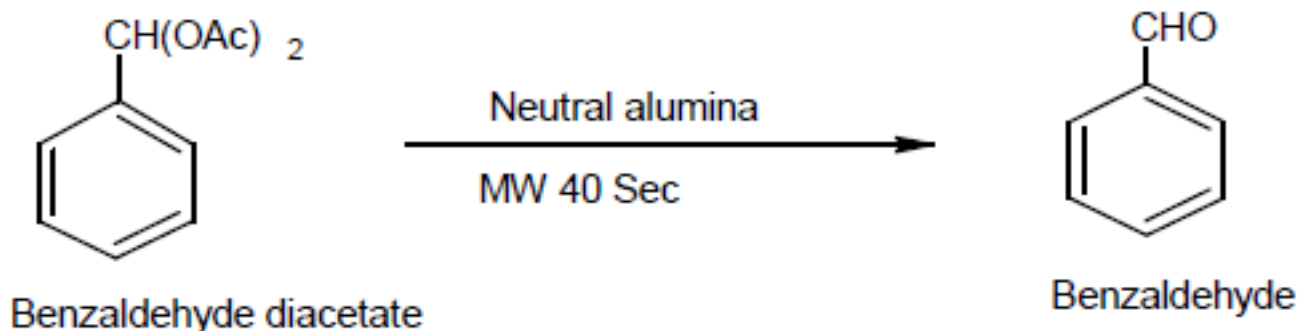
## Aromatic Nucleophilic Substitutions



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-triarlyoxytriazines 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**.

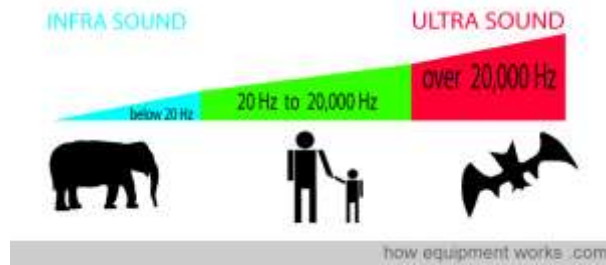
## Advantages

- 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.

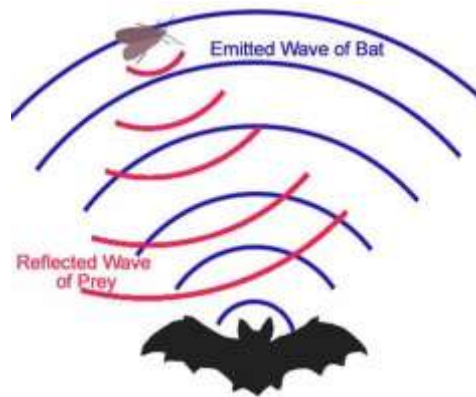
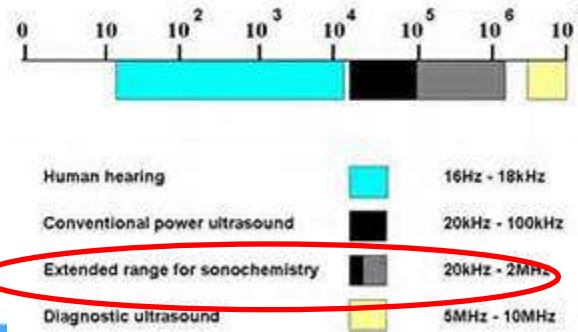
Ultrasound echoes can be used to measure distance (e.g. sonar) and to see inside objects (scans).

**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.



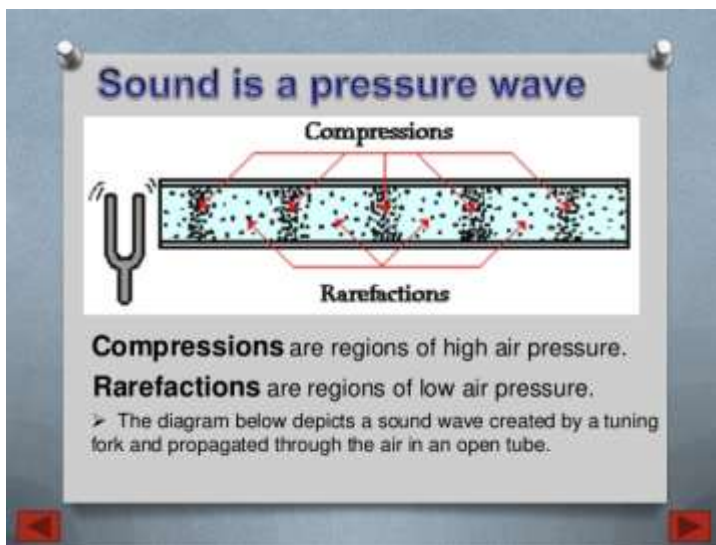
## THE FREQUENCY RANGES OF SOUND



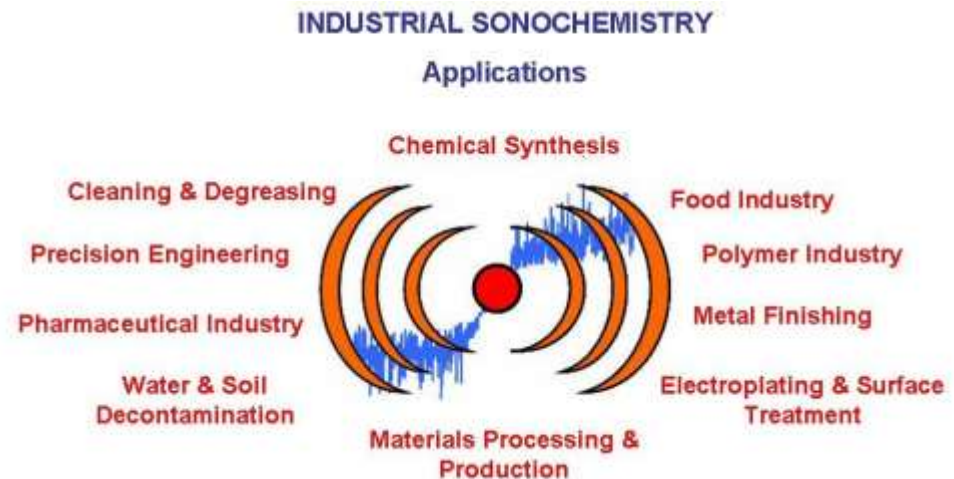
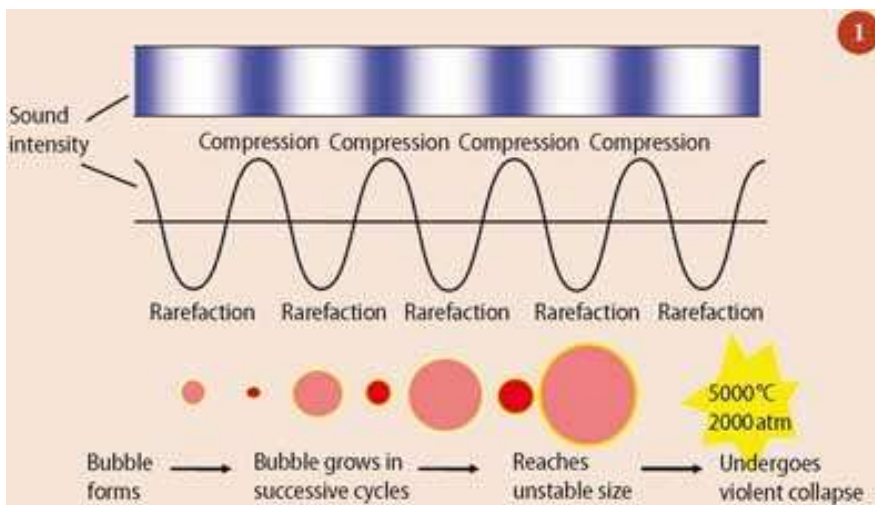
- Ultrasound refers to sound waves with frequencies higher than those detectable by the human ear, i.e. around **18 kHz**.
- The ultrasound frequencies of interest for chemical reactions (typically **20-100 kHz**) are much lower than used for medical applications (**3-10 MHz**).



# Ultrasound

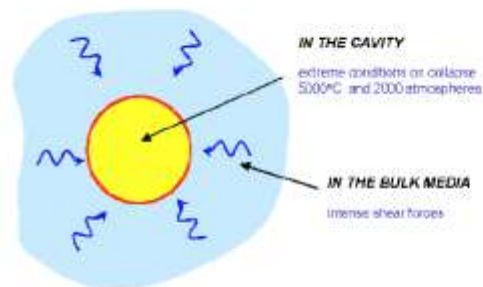
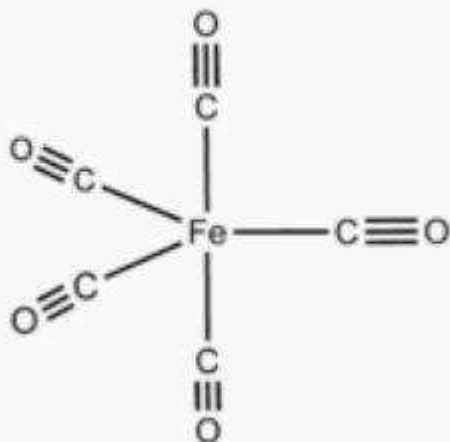


- A sound wave is propagated by a series of compression and rarefaction cycles. When it passes through a liquid medium, it causes the molecules to oscillate around their mean position, **the average distance between molecules is reduced and, conversely, it is increased during rarefaction.**



- 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.**

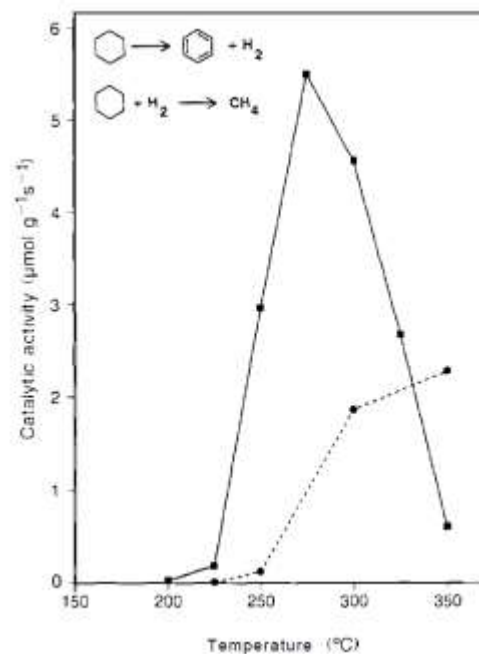
## Iron pentacarbonyl



Acoustic cavitation in a homogeneous liquid

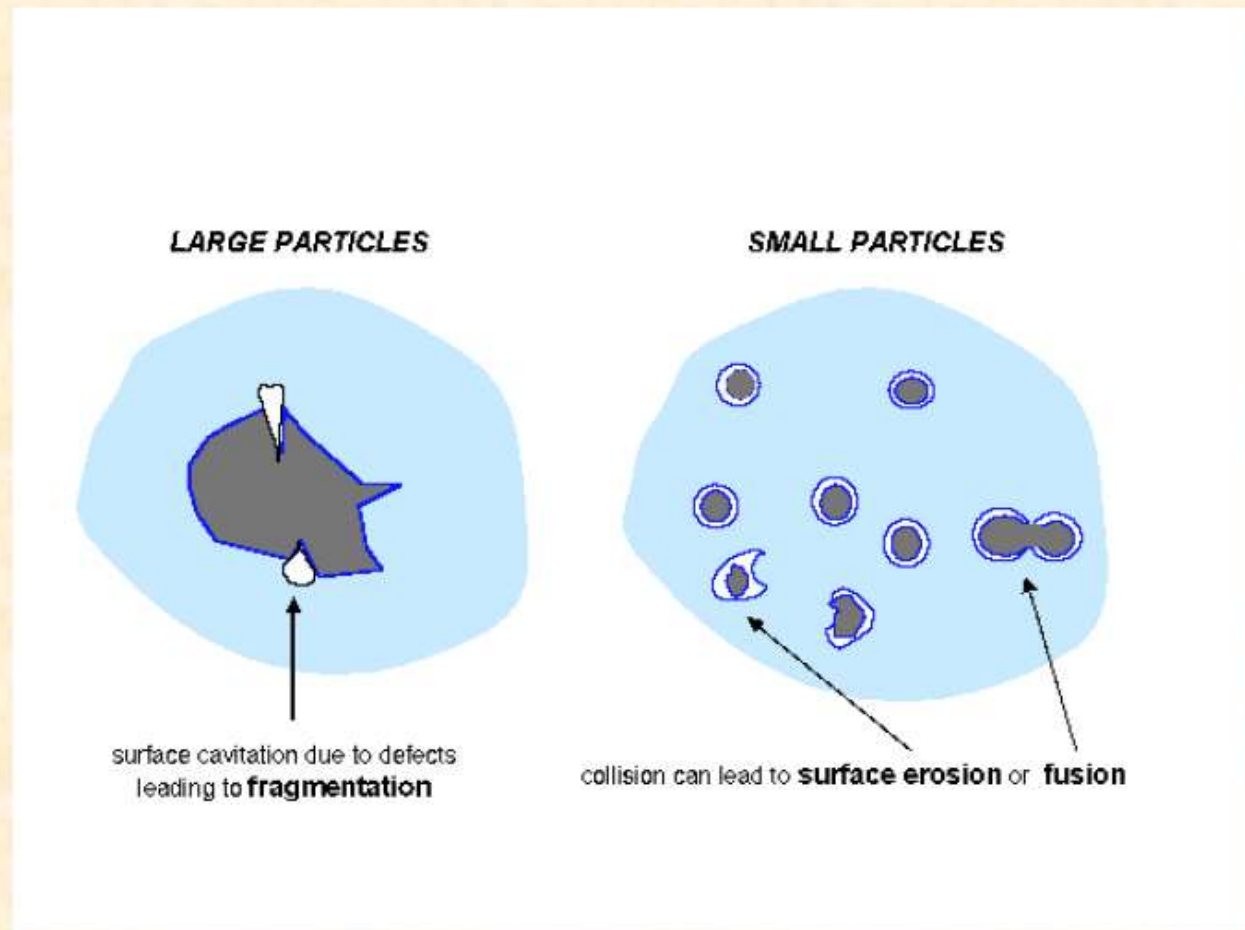


Suslick - ~ 4-5000 K



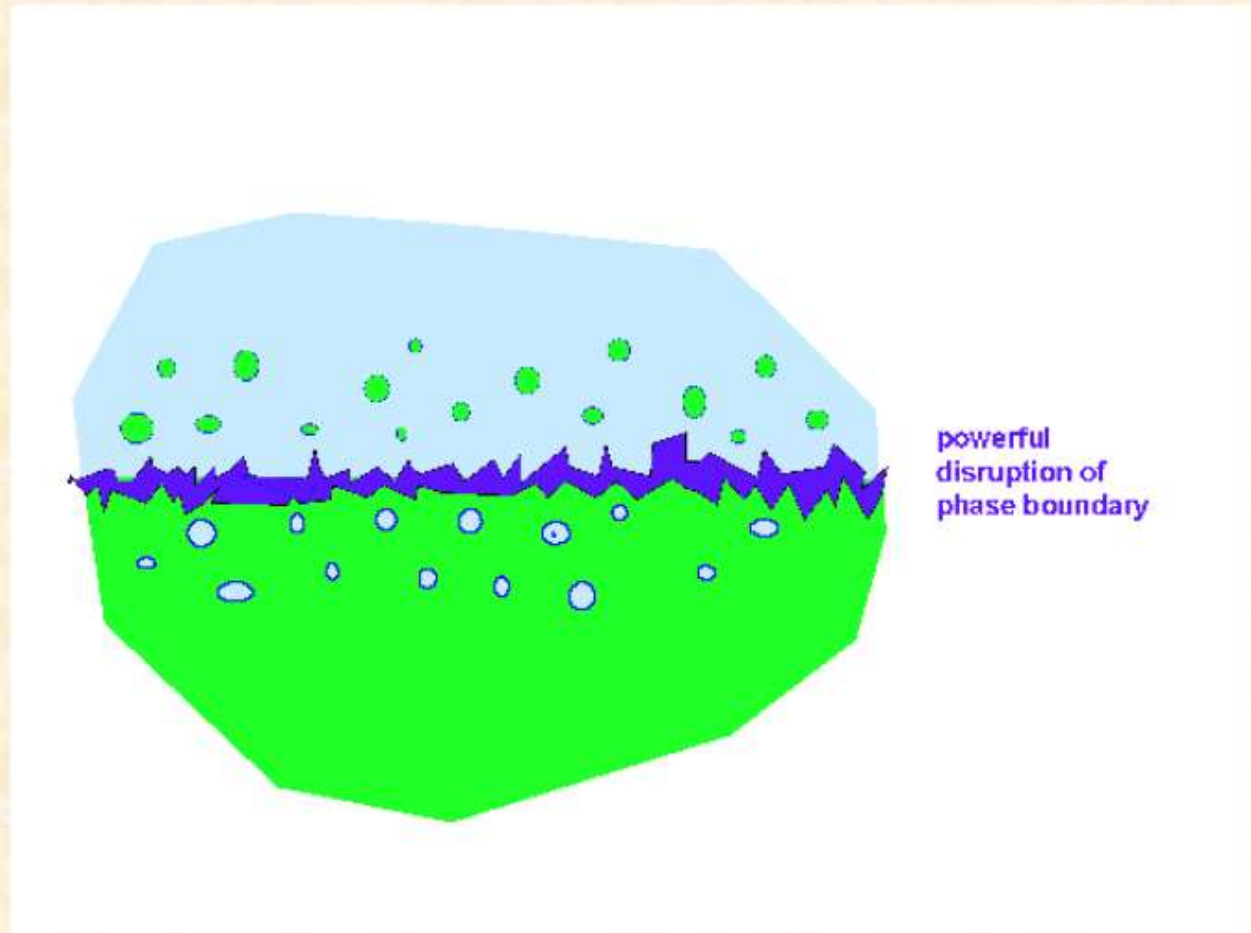
Suslick K.S., Choe S-B., Chichowlas A.A. and Grimstaff M.W. (1991) Nature, **353**, 414

# Ultrasonics/Sonochemistry – Acoustic Cavitation



Acoustic cavitation in solid/liquid system

# Ultrasonics/Sonochemistry – Acoustic Cavitation

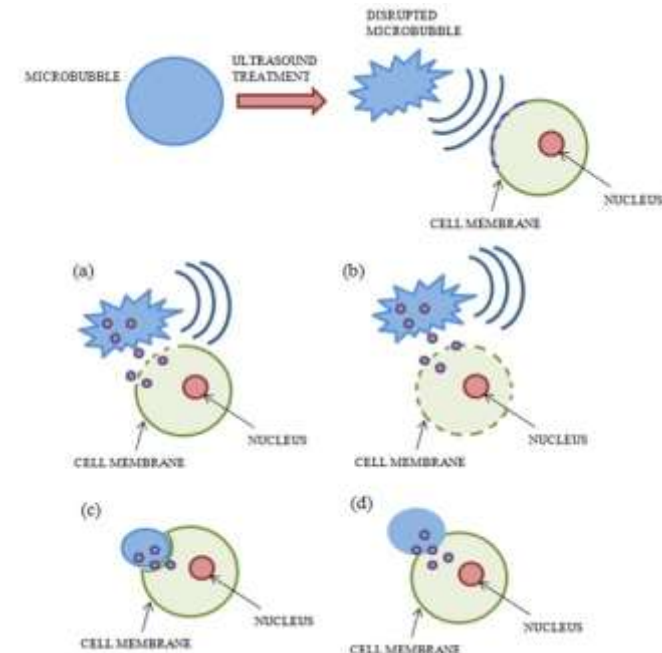
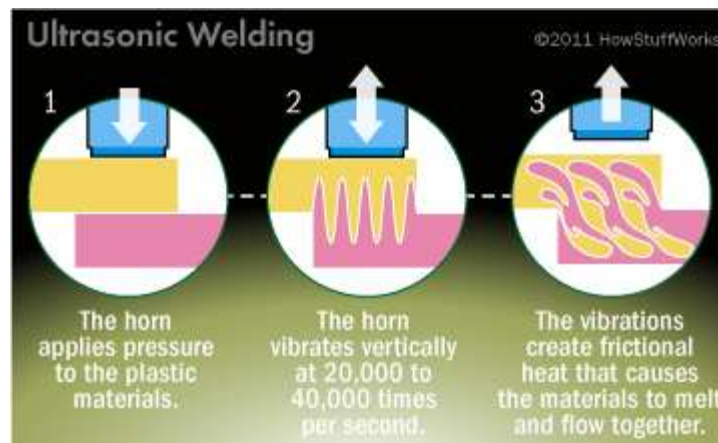


Acoustic cavitation in liquid/liquid system

# Ultrasound

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

Application	Examples
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

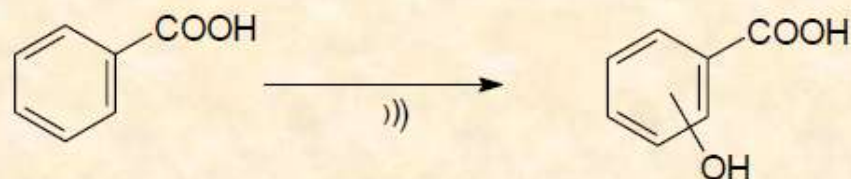
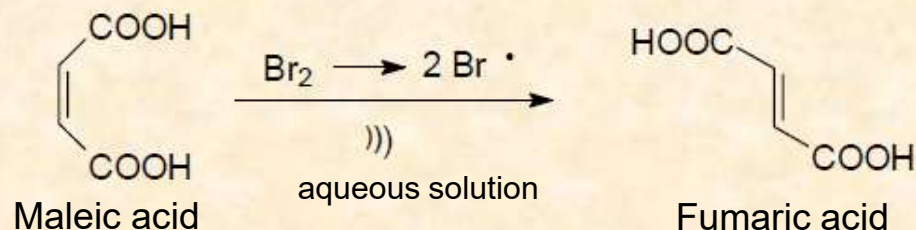
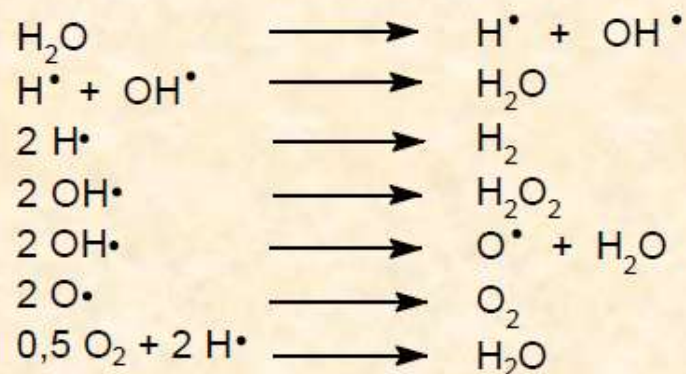
- Phase Transfer Catalysis
- Reactions with metals
- Heterogeneous Catalysis

### 3. Enzyme reactions

# Ultrasonics/Sonochemistry – Synthesis

## 1. Homogeneous sonochemistry

### 1.1. Aqueous sonochemistry



# Ultrasonics/Sonochemistry – Synthesis

## 1. Homogeneous sonochemistry

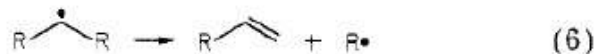
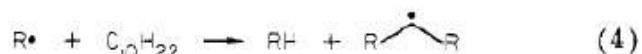
### 1.2. Non-Aqueous sonochemistry

#### Scheme 1: Rice Radical Chain Mechanism<sup>a</sup>

initiation:



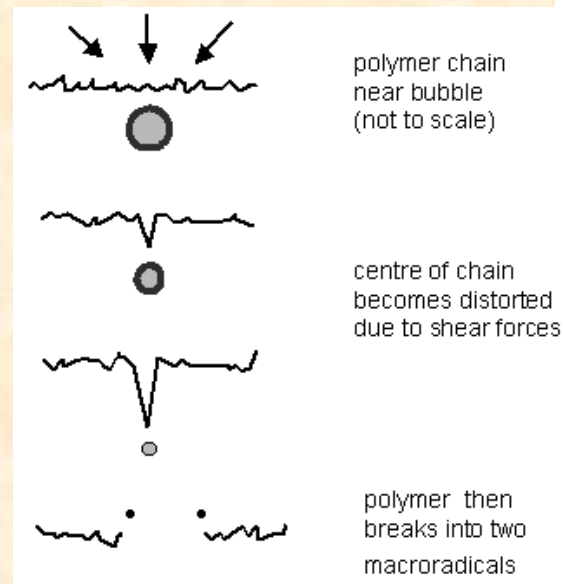
propagation:



termination:

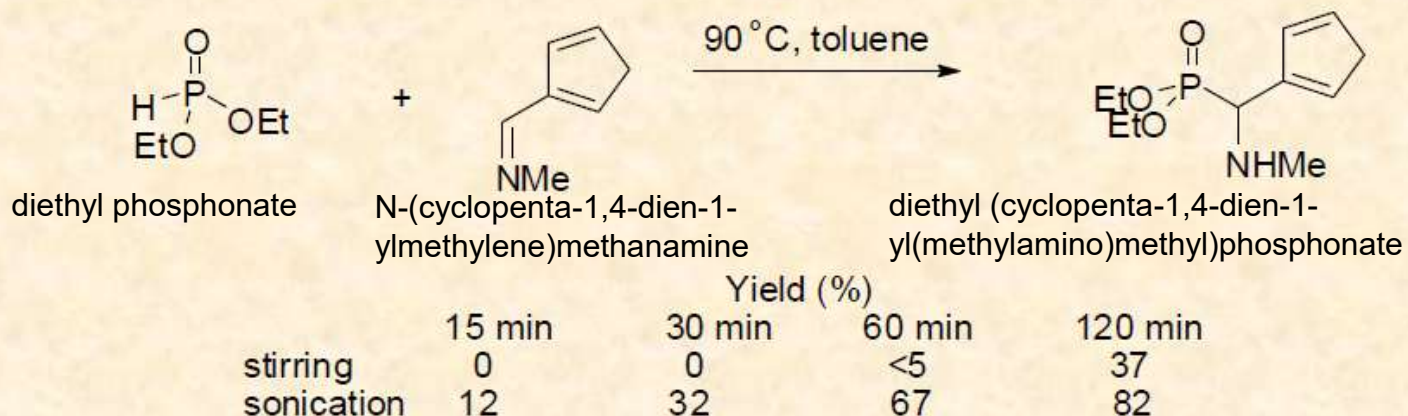


<sup>a</sup>  $\text{R}^\bullet$  = terminal radical,  $\text{R}-\dot{\text{C}}\text{H}-\text{R}$  = internal radical.



# Ultrasonics/Sonochemistry – Synthesis

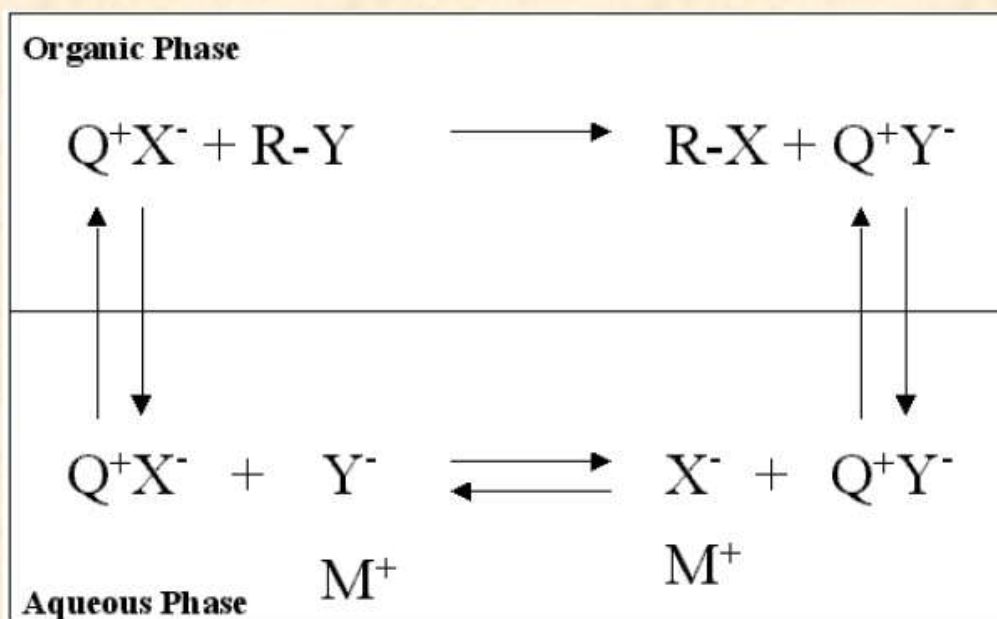
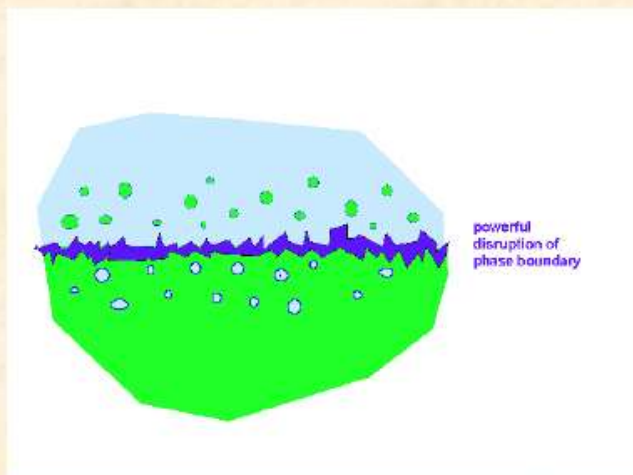
## 1.2. Non-Aqueous sonochemistry



# Ultrasonics/Sonochemistry – Synthesis

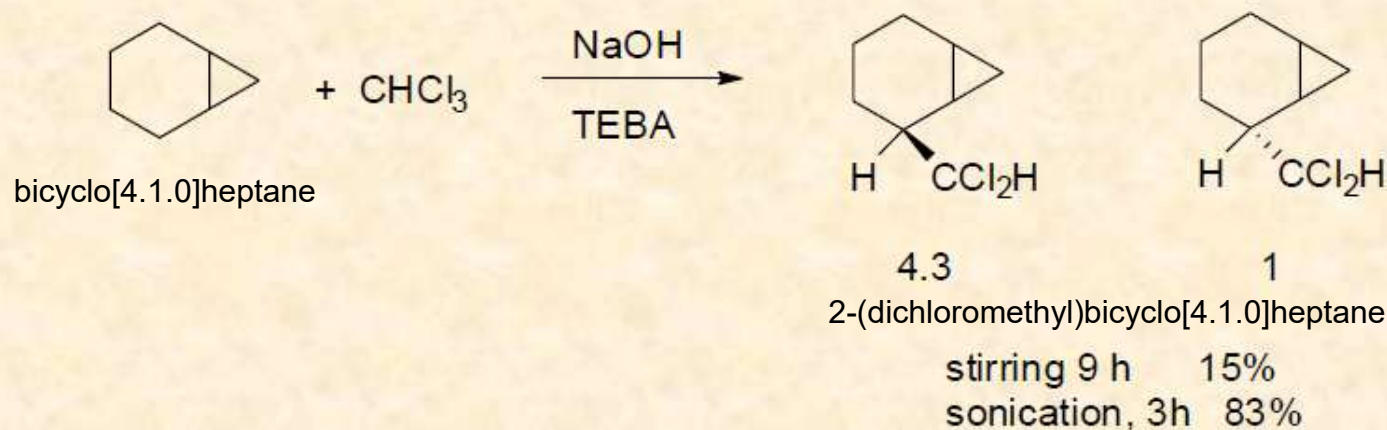
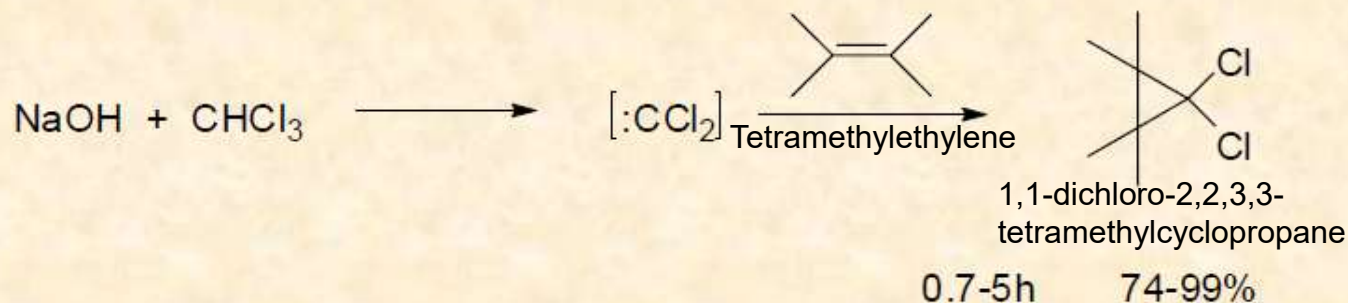
## 2. Heterogeneous sonochemistry

### 2.1. Phase transfer catalysis



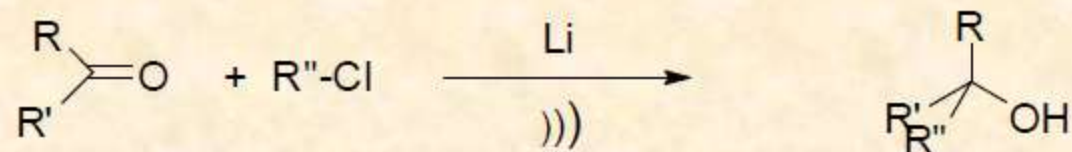
# Ultrasonics/Sonochemistry – Synthesis

## 2.1. Phase transfer catalysis

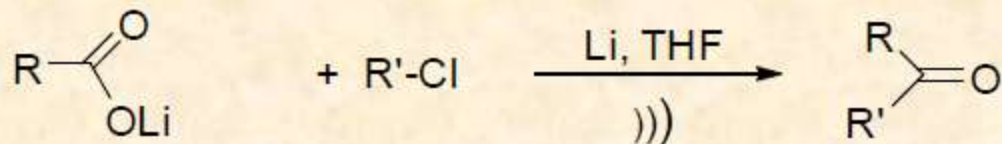


# Ultrasonics/Sonochemistry – Synthesis

## 2.2. Reactions with metals



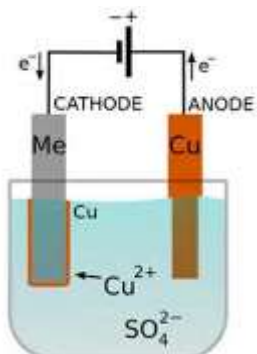
10-40 min 68-99%



72-99%

# Organic Electrochemistry

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

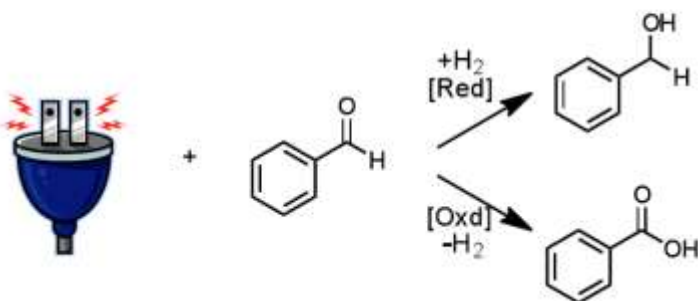


Electroplating



**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



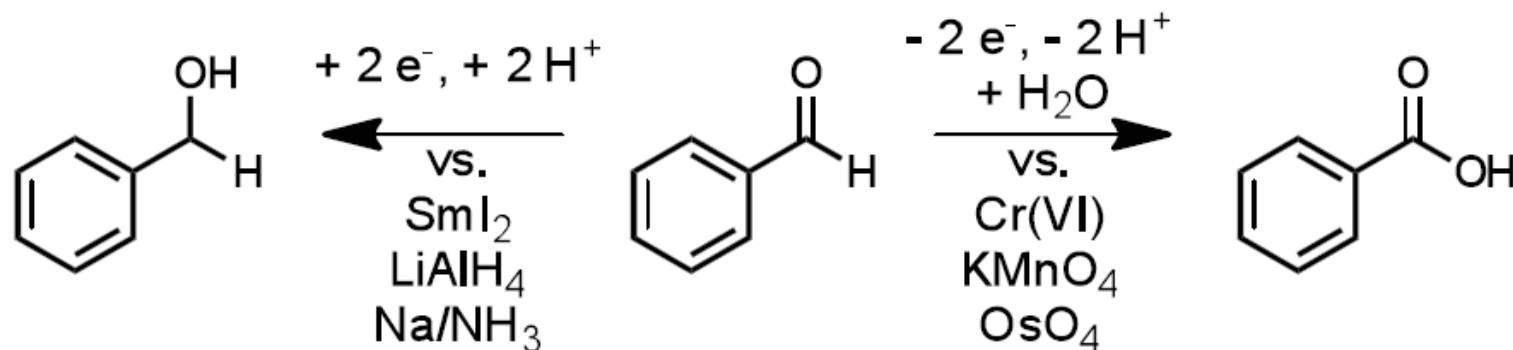
**Green benefits** of using electrochemical synthesis include

- 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



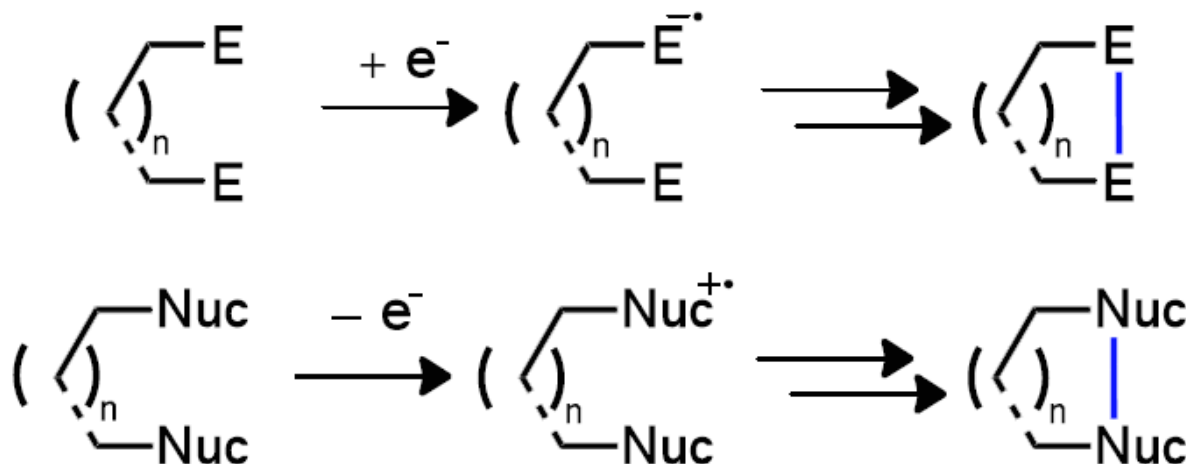
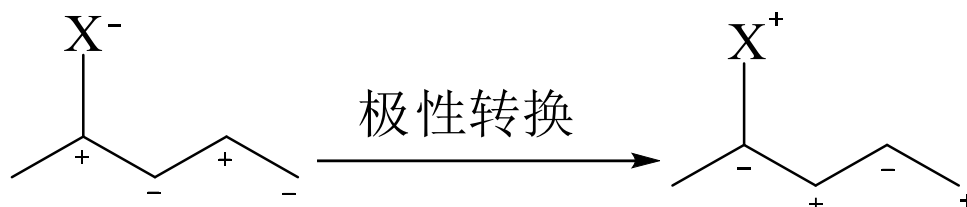
Frontana-Urbe, B.A. *et al Green Chem.* **2010**, *12*, 2099-2119.

# Organic Electrochemistry: Why?

## □ Synthetic utility

### ▣ Umpolung chemistry

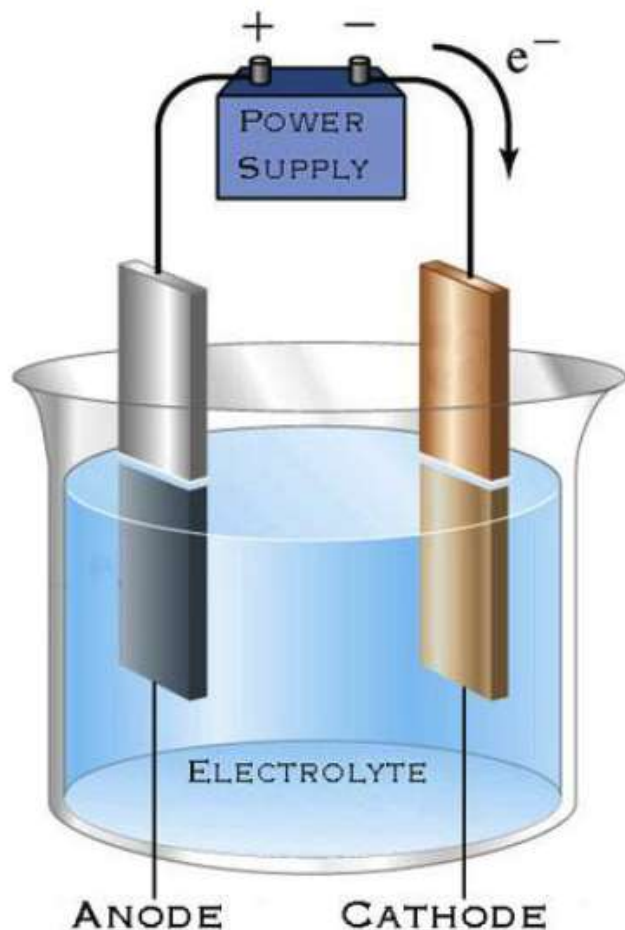
### ▣ High, typically predictable, tolerance of functional groups



E = electrophile; Nuc = nucleophile

# Electrochemistry: Basics

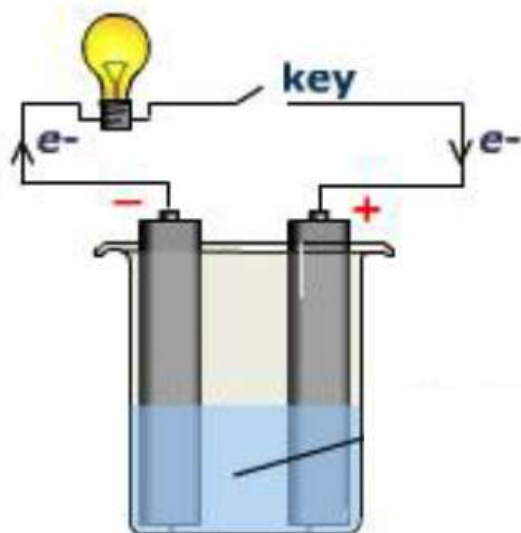
## □ Electrolytic cell - electricity is applied



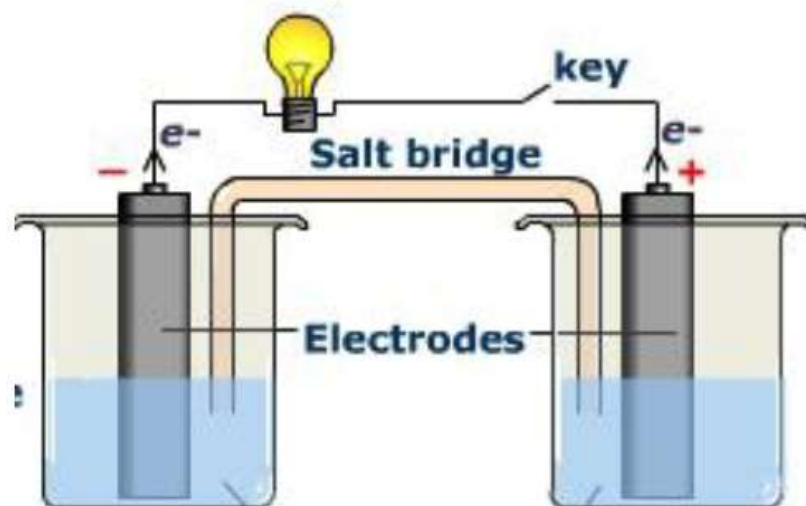
- Anode: Oxidation site
- Cathode: Reduction site
- Solvent: MeOH, CH<sub>3</sub>CN, H<sub>2</sub>O
- Electrolyte: Bu<sub>4</sub>NBF<sub>4</sub>, LiClO<sub>4</sub>, Et<sub>4</sub>NClO<sub>4</sub>
- Two methods for actions:
  - Constant current
  - Constant potential
- $\Delta G = -n F E$

# Electrochemical Cell: Design

- Two main types of cells:



Undivided



Divided

# Electrochemical Cell: Design - Undivided



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

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

Wright, D. L., et al *Chem. Soc. Rev.* **2006**, 35, 605-621

# Electrochemical Cell: Design - Divided



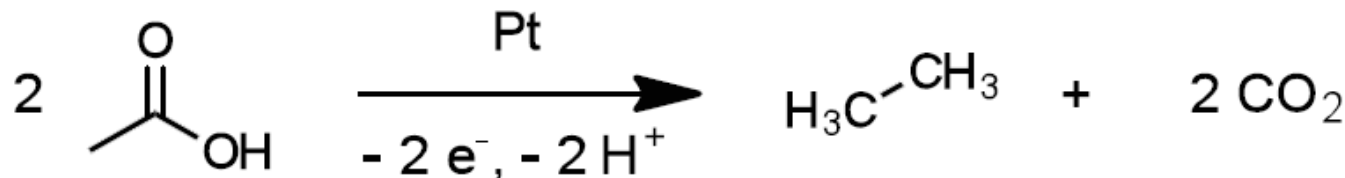
<http://www.blogs.uni-mainz.de/fb09akwaldvogel/files/2010/09/oximered2a2.jpg>

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

# Organic Electrochemistry: Early Beginnings

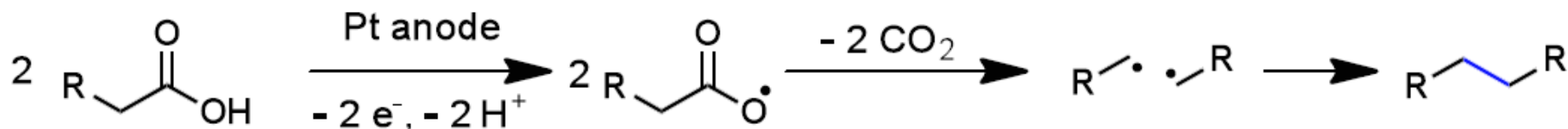
6

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



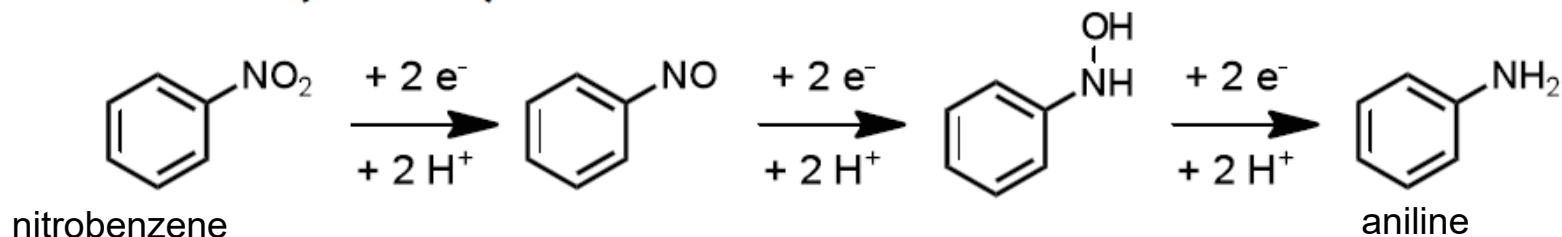
Faraday, M. *Phil. Trans. R. Soc. Lond.* **1834**, 124, 77-122.

## □ Kolbe Electrolysis (1848):



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

## □ Haber (1900):

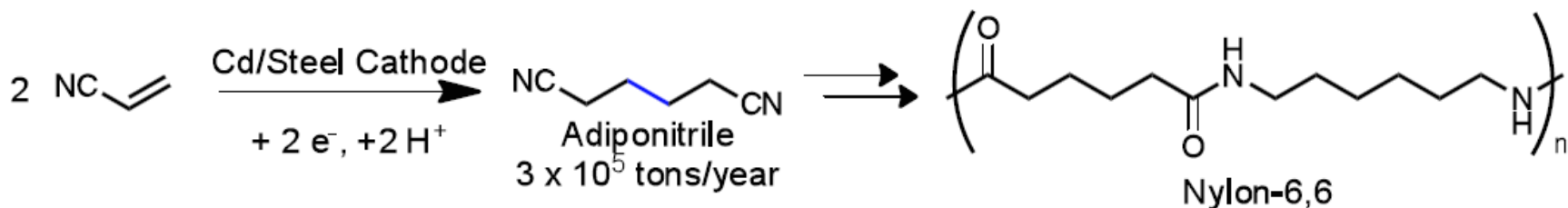


Haber, F. et al. *Z. Phys. Chem.* **1900**, 32, 271.

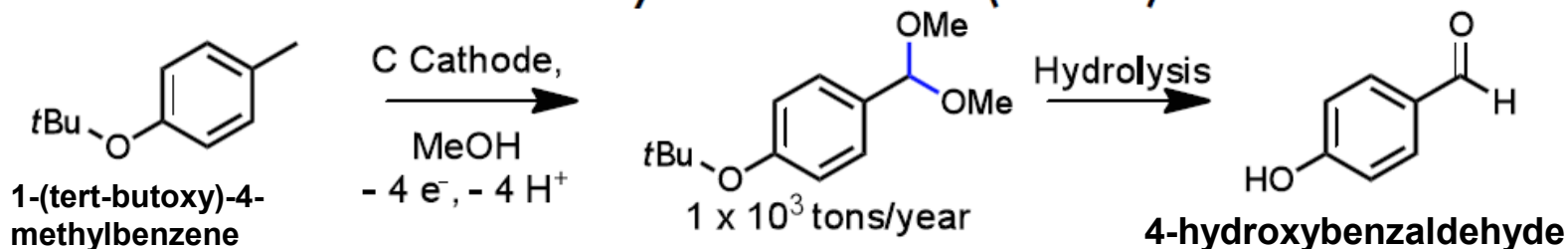
# Organic Electrochemistry: Use in industry

7

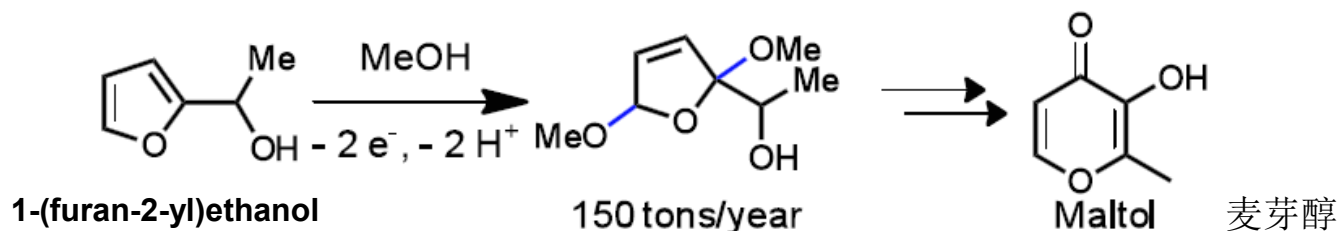
## □ Hydrodimerization of Acrylonitrile (Monsanto):



## □ Oxidation of Methyl Aromatics (BASF):

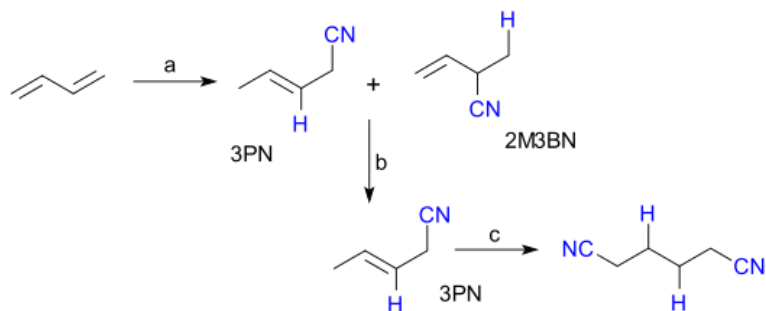


## □ Methoxylation (Otsuka):

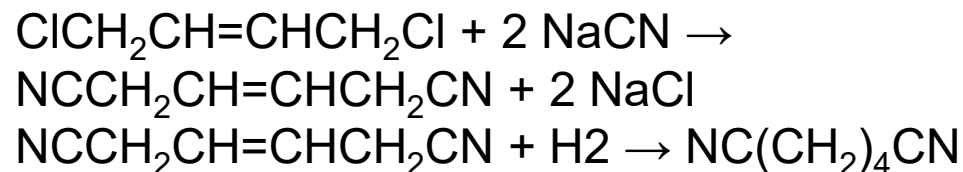


Pletcher, D.; Walsh, F. C. Industrial Electrochemistry; Blackie Academic & Professional: Glasgow, 1993

# Nickel-catalysed hydrocyanation of butadiene

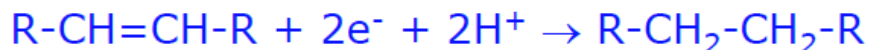


- The majority of adiponitrile is prepared by the **nickel-catalysed hydrocyanation of butadiene**, as discovered at DuPont.
- The first step involves monohydrocyanation affording isomers of pentenenitriles as well as 2- and 3-methylbutenenitriles.
- In the final stage, these pentenenitriles are subjected 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 involves the applications of NaCN, which is **highly toxic**, so from the consideration of green chemistry, this process is not environmentally benign.



# Reaction types

## Additions:



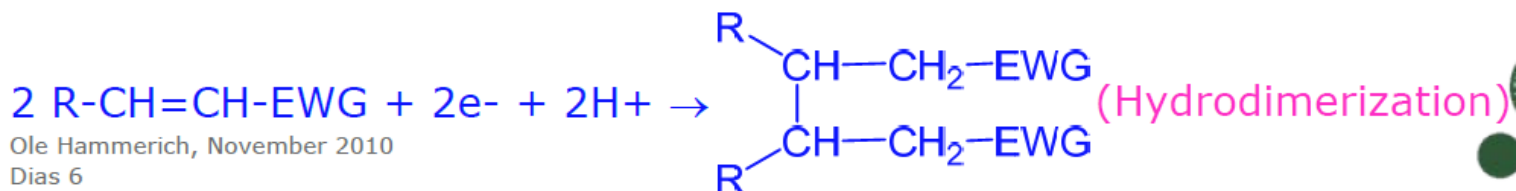
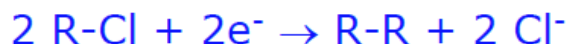
## Substitutions:



## 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, 陈彦好, 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