Light and Life: Real Life Applications of Photochemistry

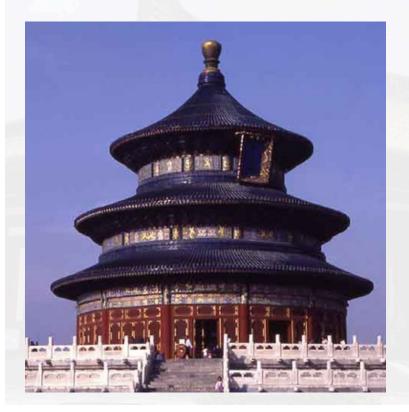


Konark





Modhera



Recognizing the importance of light, SUN-its ultimate source has been worshipped in many ancient cultures. Only a few have gone beyond to probe its nature.

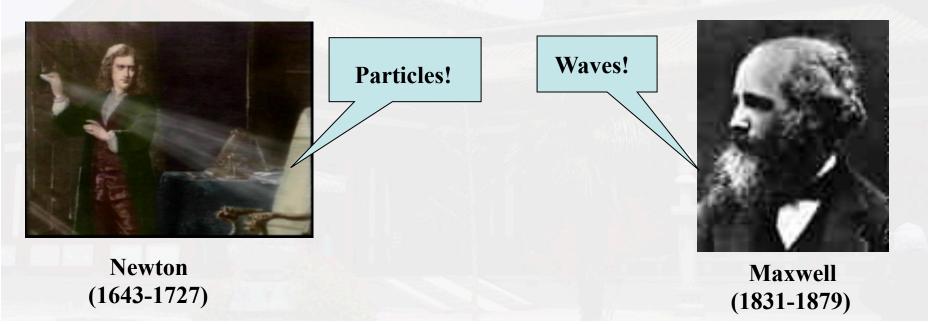
What is LIGHT?

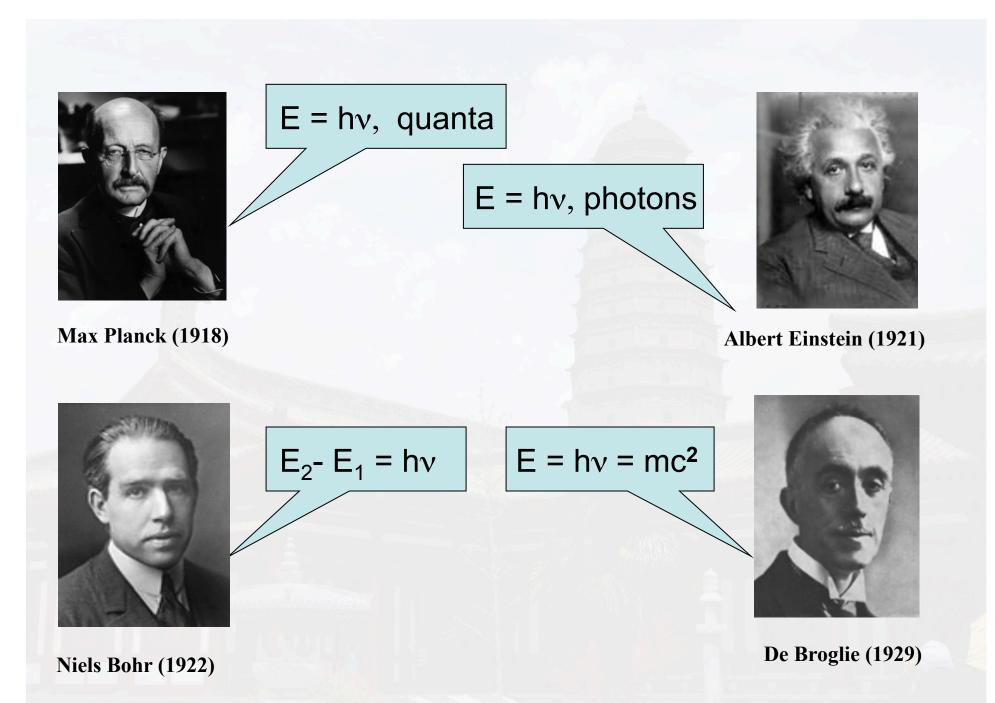




The light and heat of the sun is composed of minute particles.

Lucretius (50 BC)





Light: Prosperity through basic science



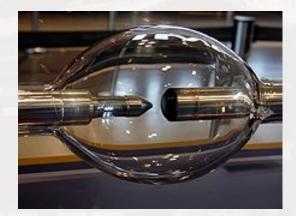
Oil lamp



Filament lamp



Fluorescent lamp



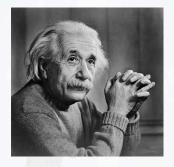
Gas arc lamp





Light emitting diodes

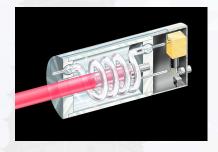
LASER (Light Amplification by the Stimulated Emission of Radiation) Invention and Innovation



1917: Albert Einstein derives the theoretical basis for the laser.



1965: The compact laser disc (CD) invented.



1960: The first working (ruby) laser.

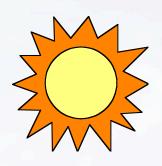


1974: A laser-driven barcode scanner used for the first time.

The world market for laser technology is now over \$ 5 trillion a year

Light and Life

- ➡> Photomedicine
- => Lithography
- Industrial Synthesis of Chemicals
- Photography, Xeorography and Holography
- Sunsscreen, Photochromic Glass
- Photostabilization
- Photocuring
- ➡ TiO₂: Environmental Cleanup
- Solar Energy Conversion



Biological Applications of Photochemistry

Photomedicine

Phototherapy - Jaundice treatment

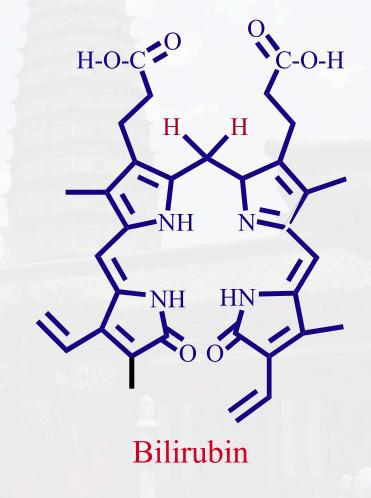
PUVA therapy - Skin disorders, Blood cancer

Photodynamic therapy - Cancer

* Lasik surgery - Vision correction

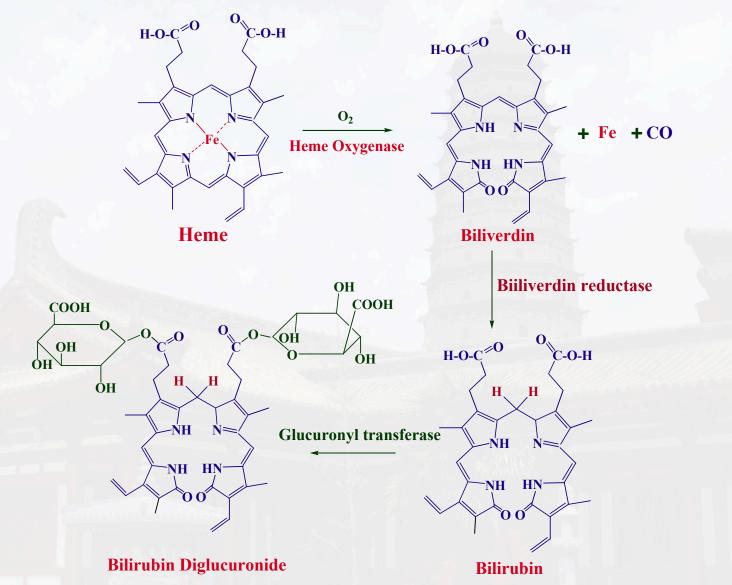
Phototherapy for Neonatal Jaundice Treatment

- Accumulation of the potentially toxic yellow liphophilic bilirubin in human serum leads to Jaundice.
- If the percentage of bilirubin increases to 15-25 mg/100 ml, it will lead to hyperbilirubinemia.
- Severe hyperbilirubinemia cases, sufficient pigment may partition into the brain to cause irreversible damage, even death.



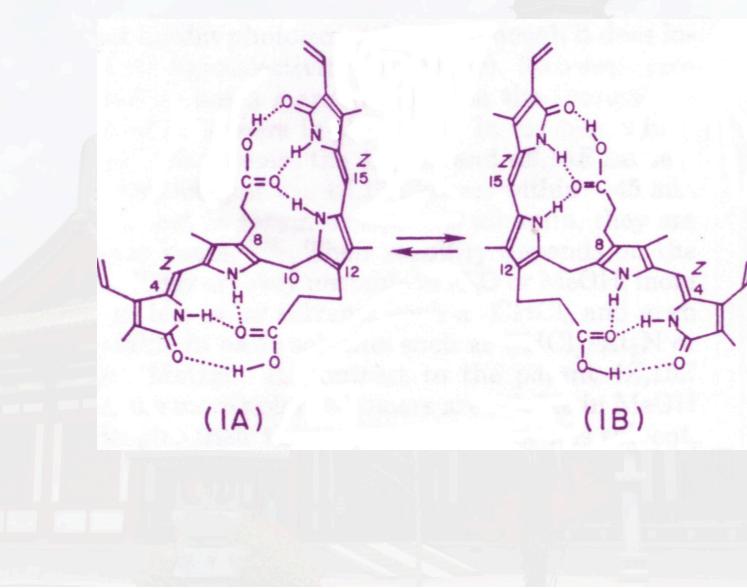
McDonagh etal., Science, 208, 1980, 145-151.

Biosynthesis of bilirubin



Glucuronyl transferase activity in fetal and new born liver is very low.

Why bilirubin is lipophilic (hydrophobic)?



Natural Cure for Jaundice





Different ways to cure jaundice

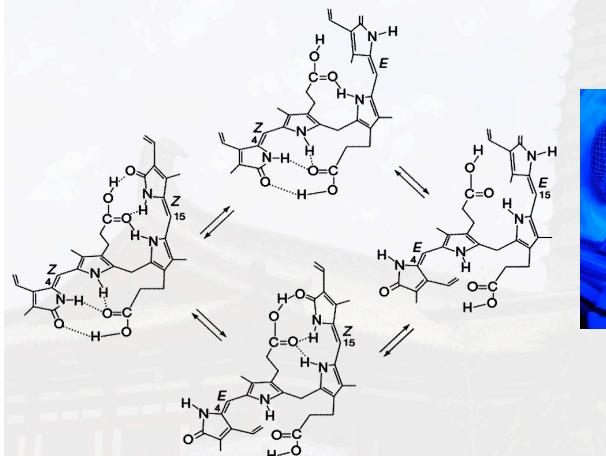
- □ Wait till liver matures soon enough to clear bilirubin unaided.
- Exchange transfusion: blood along with threatening pigment drained and replaced with clean blood.
- **D** Phototherapy irradiate the baby with light.

Discovery of phototherapy

The discovery of phototherapy stems from the observations of Sister J. Ward, a nurse in U.K.

Evening walk with hyperbilirubinemia patients - lead to discovery of phototherapy by scientists.

Phototherapy - Jaundice Treatment





"light converts bilirubin to a less hydrogen bonded (more water soluble) isomer"

Skin Disorders



Psoriasis



Polymorphic light eruption



Vitiligo



Acute dermatitis

PUVA- therapy

- **Egyptians and Asian Indians practiced this therapy centuries ago.**
- Boiled extracts of fruits of plants *Ammi majus* in Egypt and *Psoralea Corylifolia* L in India plus sunlight cured vitiligo.
- In 1988, PUVA was the first FDA (Food and Drug Administration) approved selective immunotherapy for skin disorders including cancer.

Psoralen + UVA = PUVA therapy



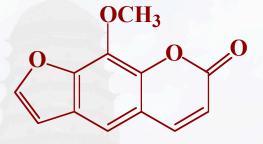


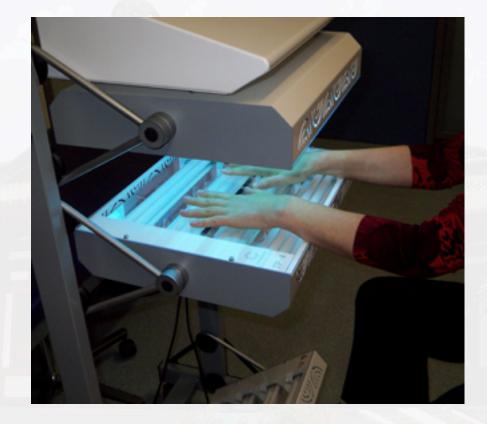
How PUVA therapy is done ?

- Methoxsalen capsules are taken two hours before exposure to UVA.
- Bath PUVA: hands and/or feet are soaked in a dilute solution of methoxsalen for 30 minutes, then exposed to UVA.
- A few patients may be treated with topical tripsor PUVA - a lotion is applied on the affected areas 10 minutes before UVA exposure.

PUVA therapy

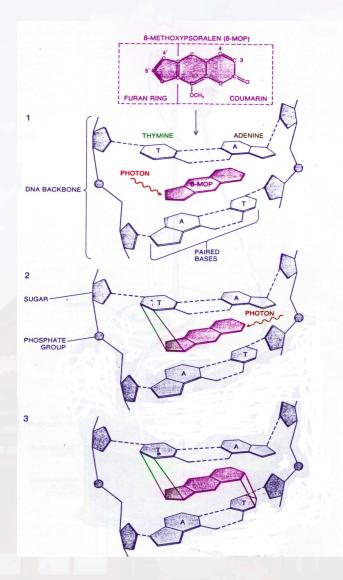
<u>**P</u>soralen + <u>Ultraviolet A</u> = PUVA</u>**







Photoadduct representation with DNA



• Intercalation

- Monofunctional adduct (3, 4 with pyrimidine base)
- Bifunctional crosslinked adduct(3, 4 and 4', 5' with pyrimidine bases)

PUVA -therapy to treat cancer

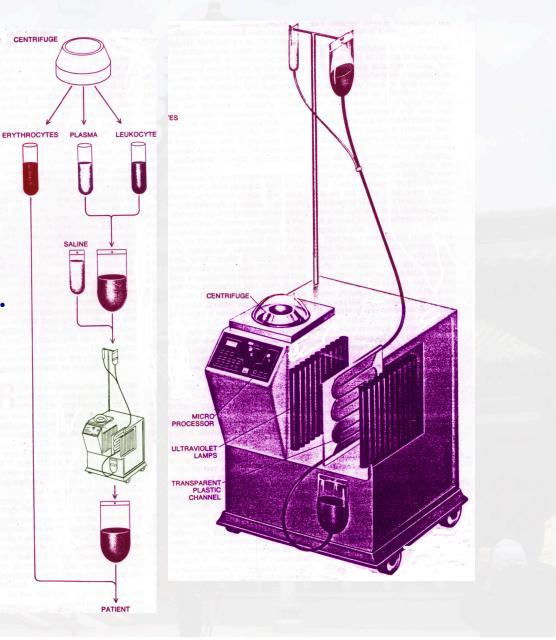
Centrifugation.

Separate white blood cells.

Drug in saline + Leukocytes.

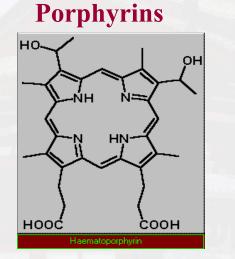
Irradiate in the machine.

Collect white blood cells.

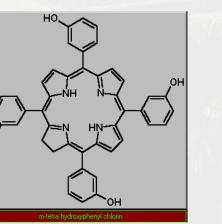


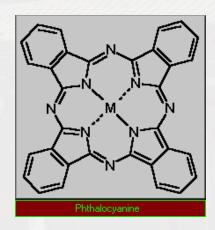
Photodynamic therapy

- **Photodynamic therapy first used in 1978.**
- □ There is currently one photodynamic drug available on the market: Photofrin.[™]
- □ Approved for the treatment of esophageal and lung cancers.



Chlorins

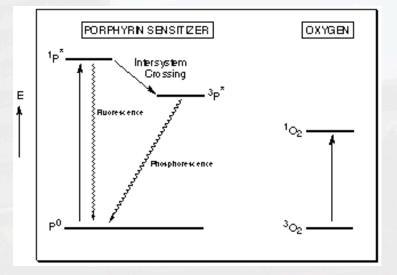


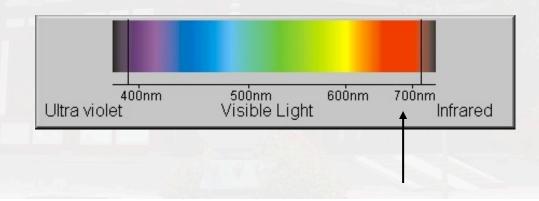


Phthalocyanines

How does photodynamic therapy work?

- PDT requires sensitizer, light and oxygen in the target tissue.
- □ Light generates reactive oxygen species.
- Reactive oxygen species can kill targeted cells either by necrotic mechanisms or by initiating the apoptotic cascade.





Ideal wavelength 650nm

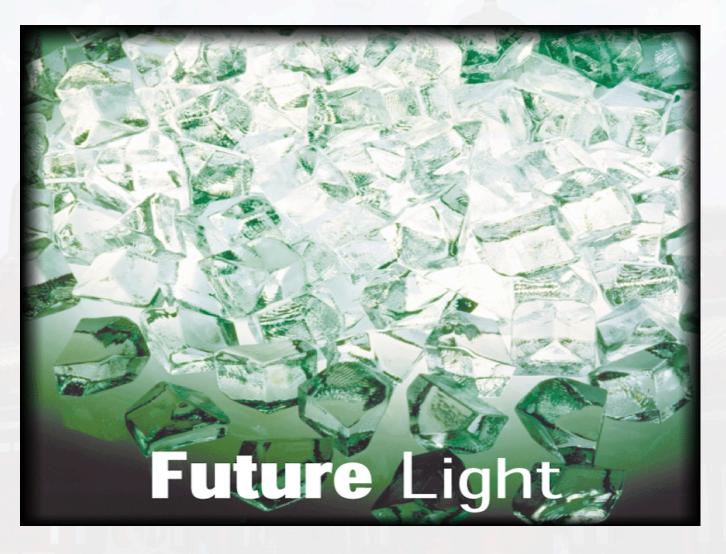
Photodynamic therapy

Laser light source Directed at target tissue

Light activated PS drug generates singlet oxygen from molecular oxygen and kills cancer cells

PDT effect kills cells

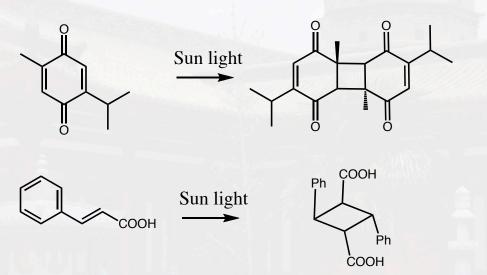
Applications of Photolithography



A reaction discovered in 19th century revolutionized the lithographic industry



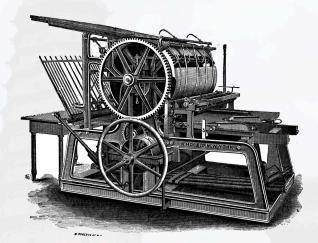
C. T. Libermann 1842–1914



Ann. Chem. Pharm. 158, 300, 1871

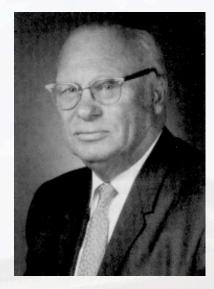
Prior to Photoresist







Photolithography: Invention 1949-50



Louis Minsk (Kodak) Polyvinylcinnamate-Based Photoressist



Otto Suess (Kalley's) Diazoquinone-Based Positive Photoressist



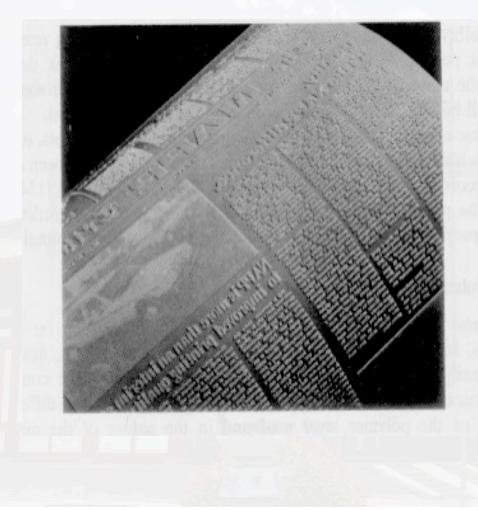
Louis C. Plambeck (DuPont) Acrylate-Based Photopolymer Imaging

Photoresist s •••• C=0 CH CH CH () Ċ=O Light +CH II CH **C=**0 C=O منہ win Radiation --- Transparency Latent image ----- Resist Developinent De velop.ment Support Developed image Negative resist Positive resist

Applications of the Principles of Photoresists and Lithography The Workhorses of Electronics and Printing

- Printing, Litho, Package, Billboards
- Color Printing
- Printed Circuit Boards (PC)
- Integrated Circuit Chips (IC)
- Photopatterning-DNA and Biochips
- Micromachines

Lithographic Printing Is the Backbone of Modern **Printing Industry**



DUPONT PROGRESS REPORT Better Things for Better Living . . . #vough Chamistry

WILMINGTON, DEL

MARCH 33, 1958

No. 2a Mid-Atlantic Edition

DU PONT DISPLAYS PLATE AT NEWSPAPER CONFERENCE



ates for rotery and flat bed use

Plans Three Types of Photopolymer Plates

PROTOBOLYMME PICTUS PITTSEURGH, P., Mar. 13 - The Photo Products Department of E. I. du Pont de Nemours & Co. no., exhibited samples of experimental photopolymer print-ing plate today to the news-sequencia by the sample of the sample of the Mod-Allandic Newspace Mechanical Conference. These plates are composed of layer of photopolymeril banded to any of photopolymeril banded to any of photopolymeril banded args of the sample of banded args of the bander of banded args of the bander of the sample of the sample photopolymeril banded args of the bander of the sample the sample of the sample of the sample of the sample the sample of the sample of the sample the sample of the sample of the sample of the sample the sample of the sample the sample of the sampl

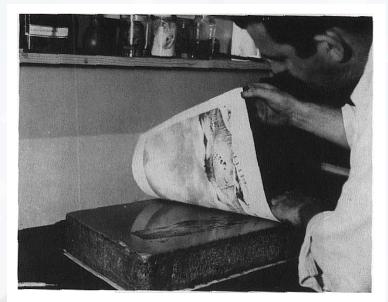
ort in Ort ciolet light exp ugh a high (right read with a dilute alks

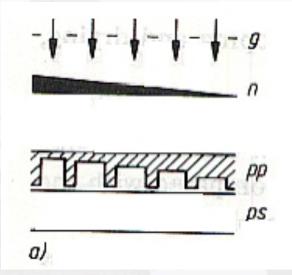
ons the sposed and unhards and unhardened or leaving the text and act at proper printing height. The exposure and wish out steps can be completed in about 15 minutes.

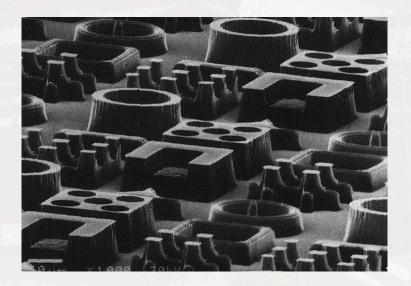
absed D minutes. A De Paul Photo Products prokerman, W. B. Vilsen, able development also can be an array plane are to ranket there years plane are to ranket the

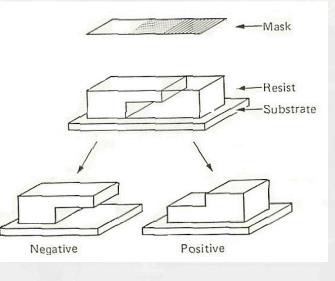


Gray Shading





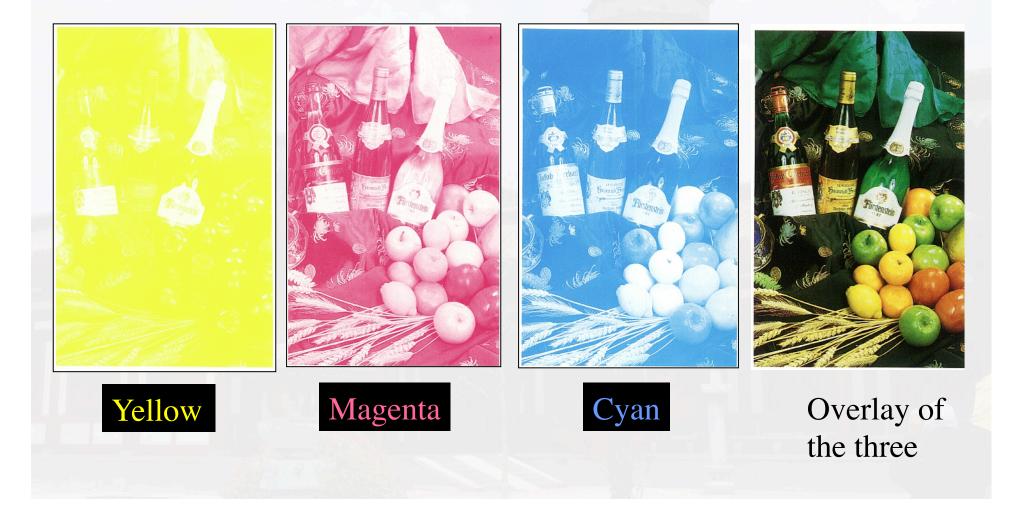




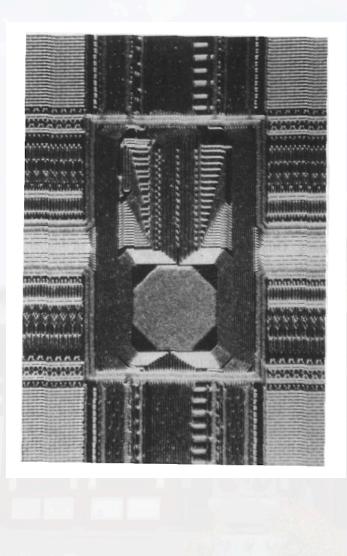
Three Color Printing

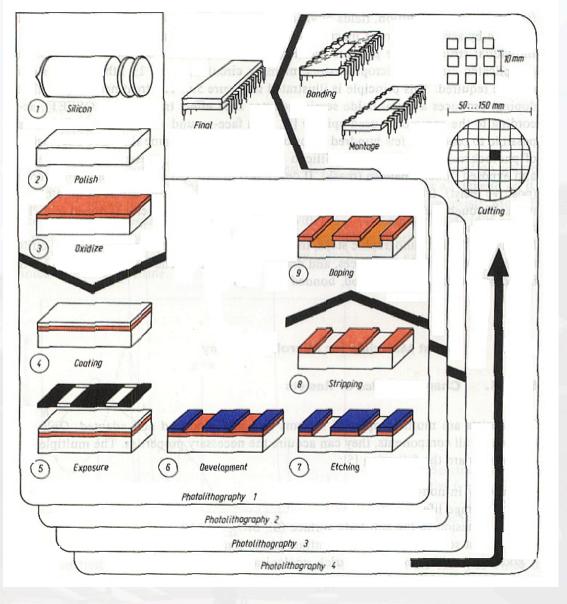
Color Printing Requires Color Separation

Color Printing is Done Through Four Color Processing



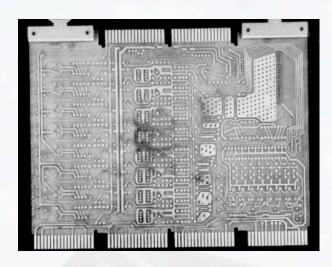
From Sand to Computer Chips

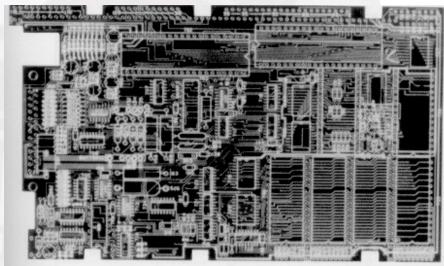


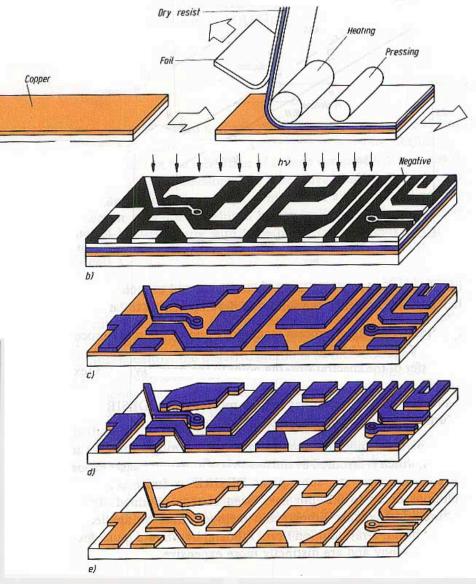


Printed Circuit Board Making

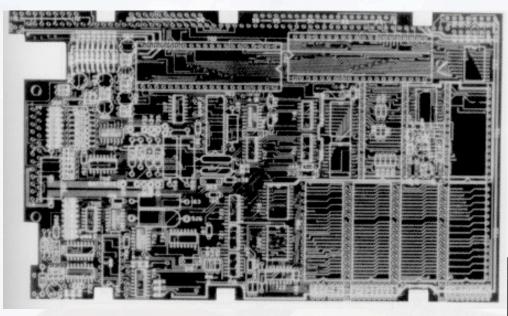
a)



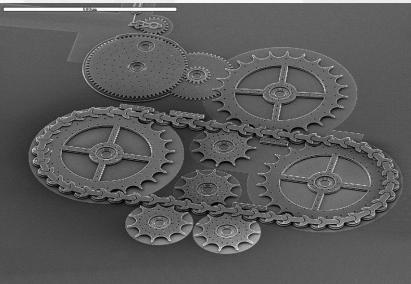




Photolithography Applications in Electronic Industry



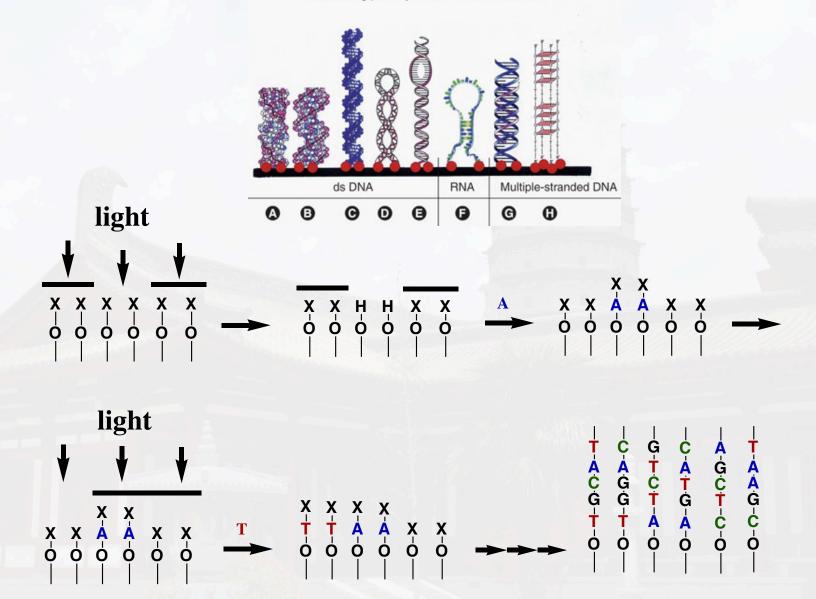
Printed Circuit Boards



Micro-Electro Mechanical Systems (MEMS)

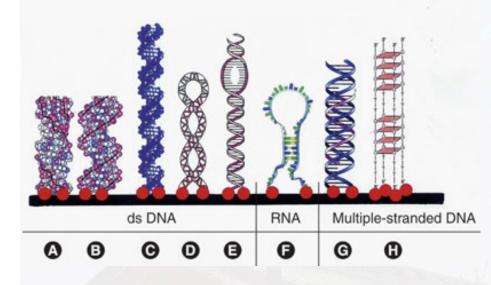
Photo Patterning-DNA Chips

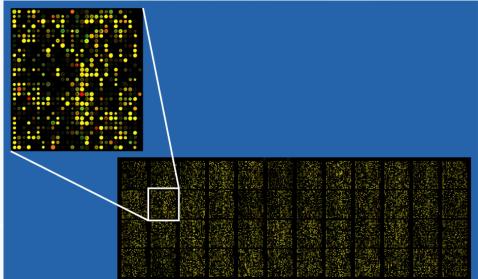
Free-floating partially immobilized nucleic acids



Biosensors Based on Photopatterning

Free-floating partially immobilized nucleic acids







Applications

- blood glucose measurements for diabetes management
- testing food for the presence of pathogenic microorganisms (*Salmonella* and *E. coli*)
- **I** sensing chemical and biological warfare agents

Lithography to Lasik Surgery



R. Srinivasan

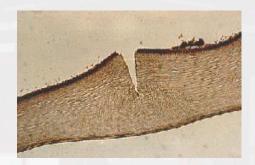


S. Blum



J. Wyne

1981: Discovery of laser ablation technique.1995: US FDA approval of human Lasik surgery.2002: Inducted into US Inventors Hall of Fame.



1981: Discovery of laser ablation



1987: Lasik surgery

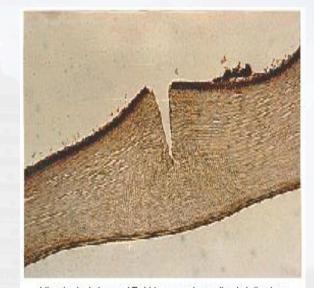
Photoablation with Excimer Lasers

Short wavelengths of light (190 to 300 nm) breaks molecular bonds (ablation)

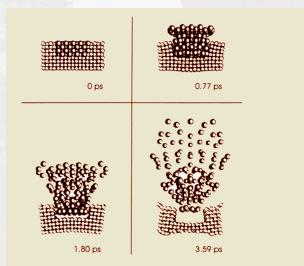
Photablation with eximer laser (eg: ArF, KrF) can be done with a micron accuracy.

Refractive surgeries

PRK – Photorefractive keratotomy LASIK – Laser assisted insitu keratomileusis



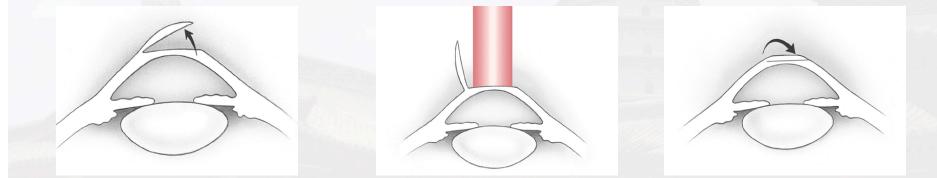
Histological photo of Rabbit cornea immediately following laser treatment.



Computer simulation of photoablation showing the movement of PMMA monomers as a function of time. Reproduced from Garrison and Srinivasan (1985) by permission. @ 1985 American Institute of Physics

How LASIK differs from PRK?

- □ LASER In-situ keratomilieusis (LASIK)
 - **First step is the lifting of corneal flap and then ablation**
 - Treatment is given beneath the flap



Brief recovery time

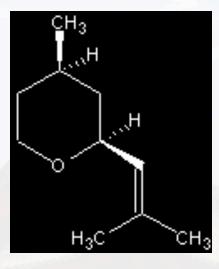
Very low infection risk and low enhancement rate

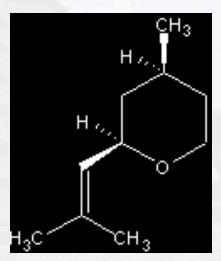
Very low risk of scarring and minimal discomfort



Photochemical synthesis of Rose oxide Photochemical synthesis of Vitamin – D Photooximation – Synthesis of caprolactam Photochlorination

Rose oxide





(4r,2s)-(-)-cis-roseoxide

floral green with clean sharp, light, rose green note, diffusive, strong (Matsuda); also has been described as powerful fruity.

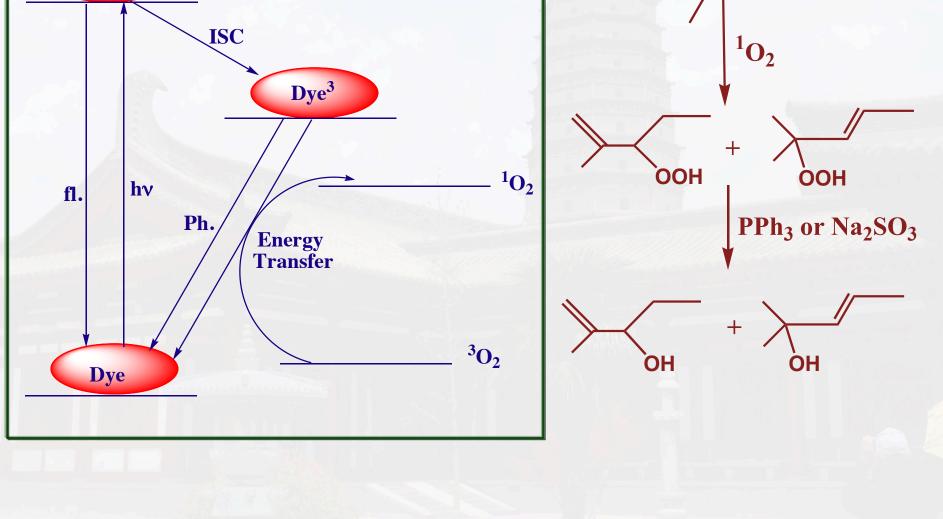
Odor Threshold = 0.5 ppb

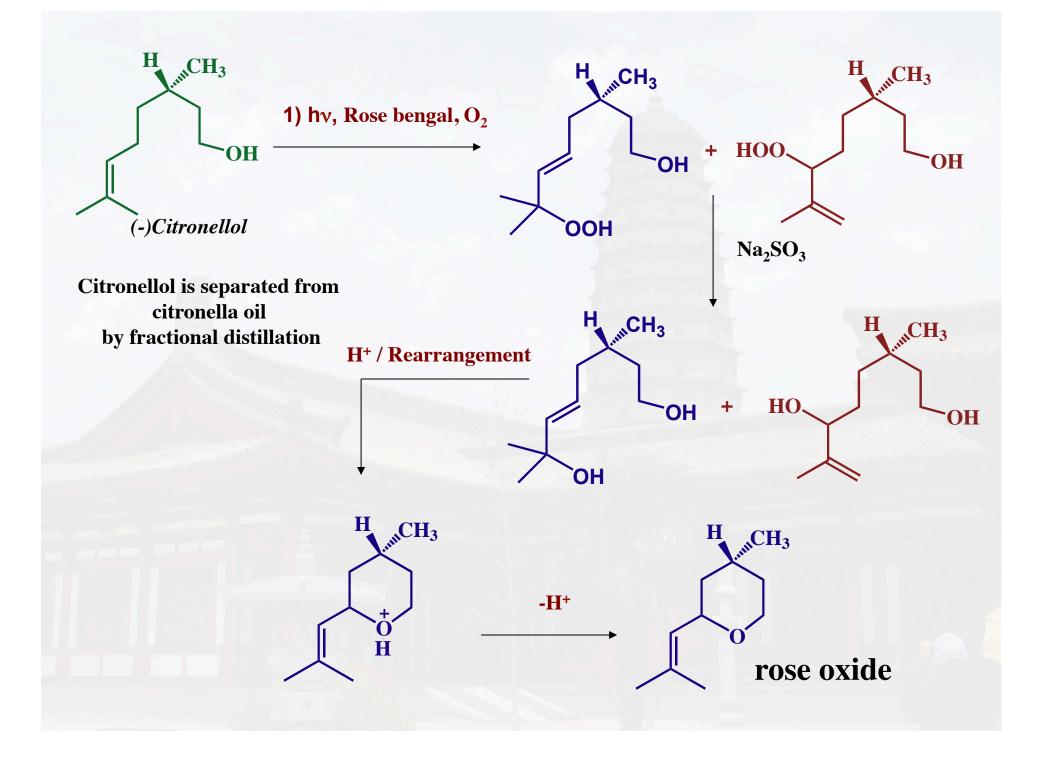
(4s,2r)-(+)-cis-roseoxide

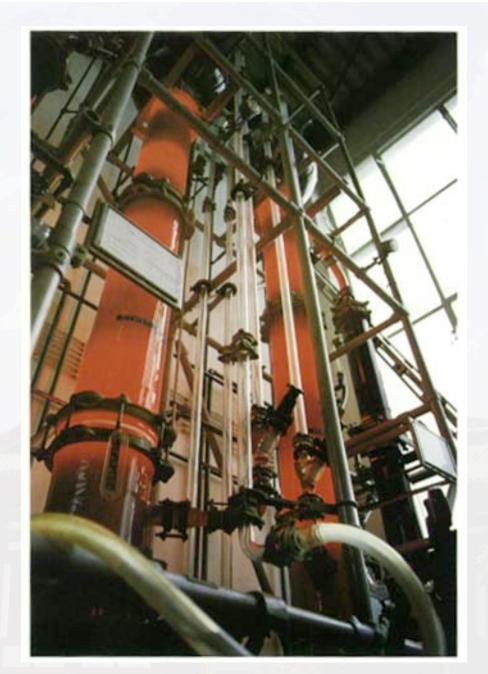
herbal, green floral, hay green, earthy, heavy (Matsuda); also has been described as sweet, floral

Odor Threshold = 50 ppb





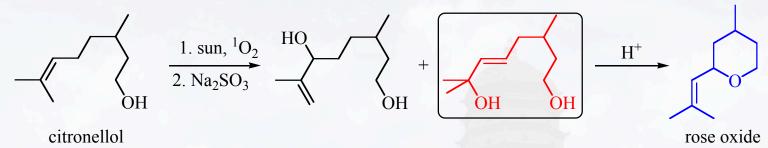




Photograph of the cylindrical immersion type reactors used by Dragoco for the production of (-)-rose oxide

The reactor is about 3 m tall, and is equipped with a 5 k W light source.

Scanned from Photochemical technology, Braun, A. M., Maurette, M-. T., Oliveros, E.



citronellol



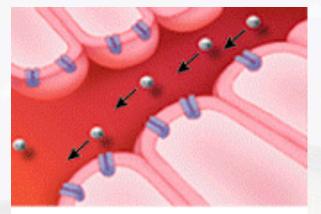




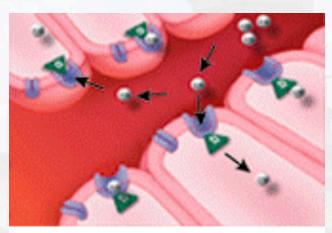


Courtesy of Prof. M. Oelgemöller

Vitamin D is absolutely necessary for the efficient absorption of calcium and phosphate from our diet



Without vitamin D, the calcium passes through the digestive system unused.

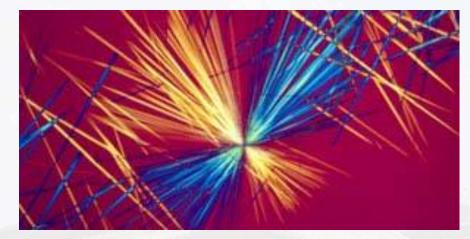


Vitamin D is essential for the body's absorption of calcium.



Child with rickets

At the present time almost all milk sold commercially in the United States has 400 IU of chemically synthesized vitamin D_3 added per quart.



vitamin D₂ (ergocalciferol: plant origin) vitamin D₃ (cholecalciferol: animal origin).

Vitamin D crystals

Commercially synthesized by Roche-Vitamins

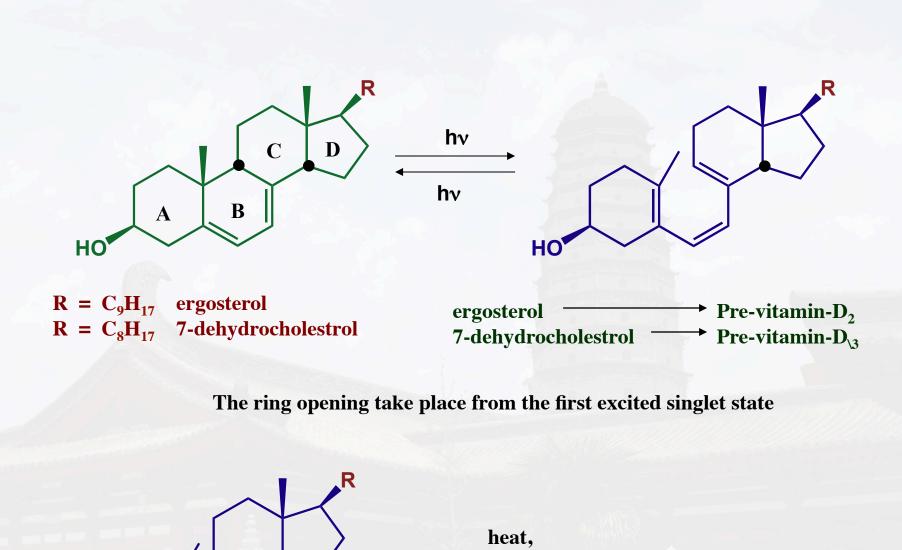
Commercial production of vitamin D_{3:}

a) 7-dehydrocholesterol

Extracted from animal skins (cow, pig or sheep) followed by an extensive purification.

b) cholesterol.

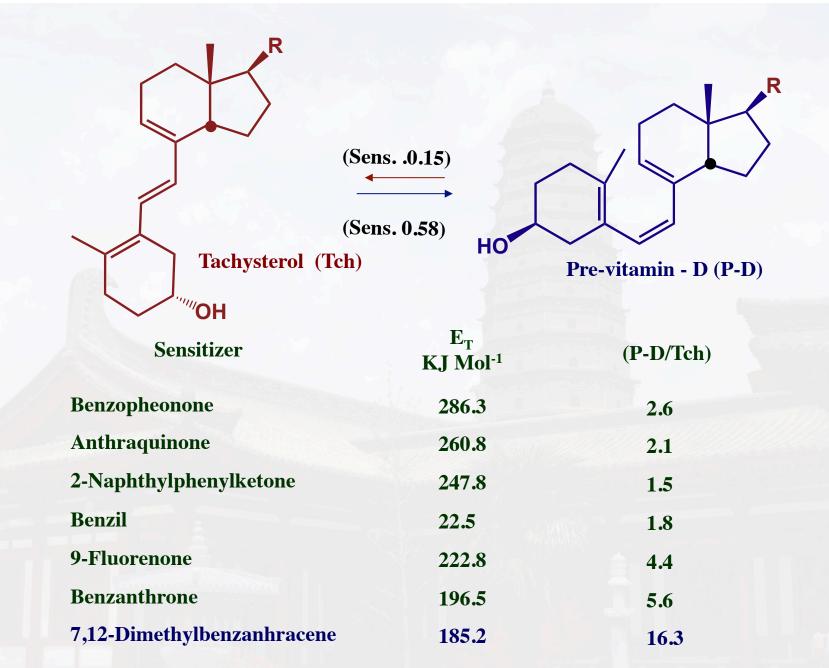
Extracted from the lanolin of sheep wool and can be converted to 7-dehydrocholesterol.



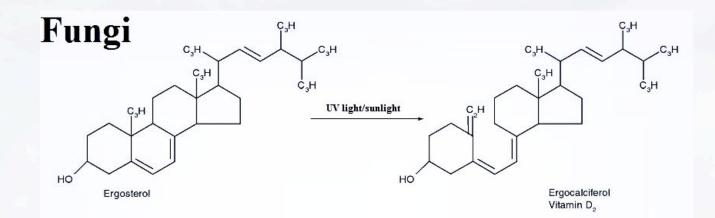
moderate temperature

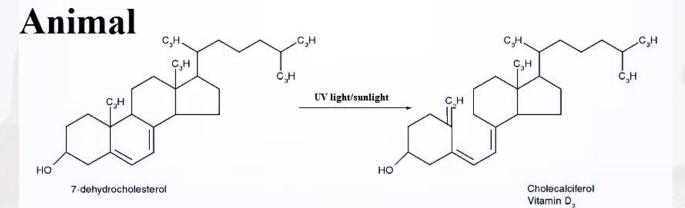
HO

Vitamin D



Initial ratio (P-D/Tch)= 0.5; solvent=ethyl ether.





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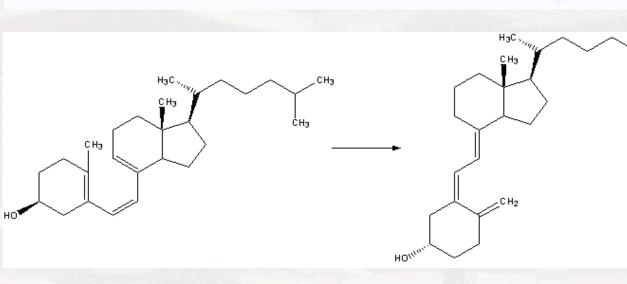


Photo-oximation of cyclohexane - industrial synthesis of *caprolactam*

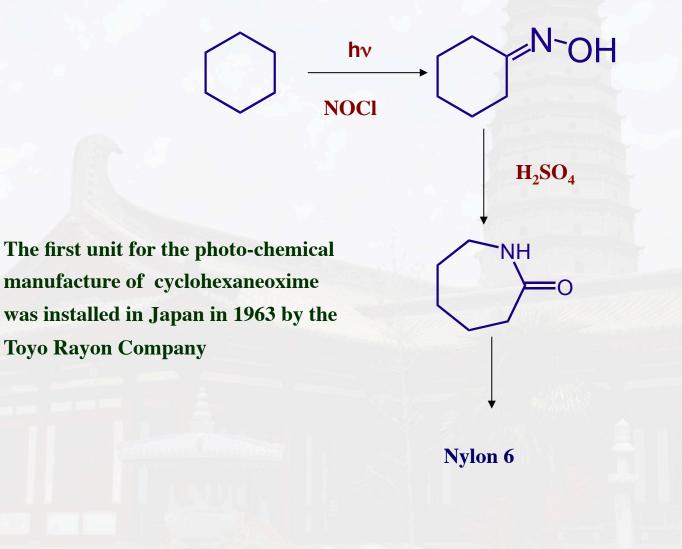
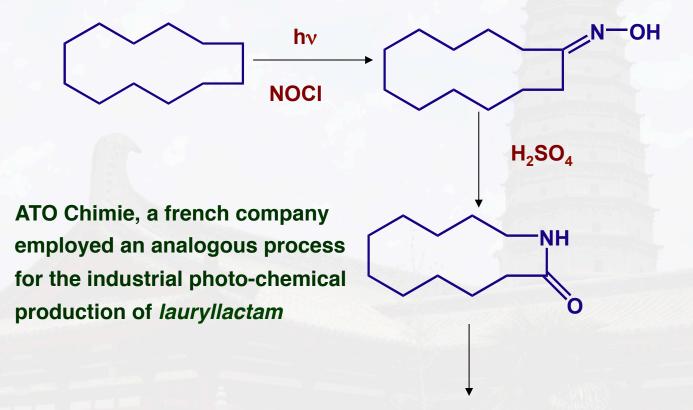


Photo-oximation of cyclododecane – industrial synthesis of *lauryllactam*



Nylon 12

Photochemical technology, Braun, A. M., Maurette, M-. T., Oliveros, E.

Photo-oximation

Photo-oximation is a special case of photo-nitrosylation.

Accidentally discovered by Lynn in 1919.

Important use in industrial application.

Tessenderlo's chemicals platform in Limburg, Belgium.



Investment, totals ~ FRF 170 million

Photochlorination

The photochlorination plant produce

a)15,000 tonnes of benzyl chloride and benzylidene chloride.

b) 7,000 tonnes of benzaldehyde.

These are some new addition to its range of synthetic organic products.

New chlorinated toluene derivatives production unit, Capacity > 60,000 tonnes a year

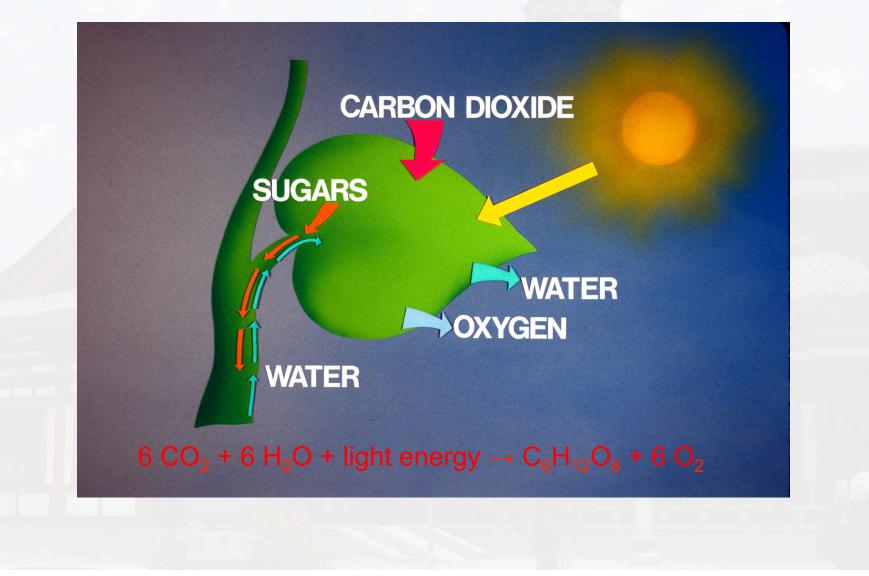
Light and Life

- ➡> Photomedicine
- => Lithography
- Industrial Synthesis of Chemicals
- Photography, Xeorography and Holography
- ➡> Sunsscreen, Photochromic Glass
- Photostabilization
- Photocuring
- ➡ TiO₂: Environmental Cleanup
- Solar Energy Conversion



Survival Strategy: Photosynthesis

Light Energy Harvested by Plants



Importance of Photosynthesis



Provides energy for plants



Provides energy for animals that eat plants



Provides energy for animals that eat animals that ate plants



Provides energy for organisms that break down all of the above



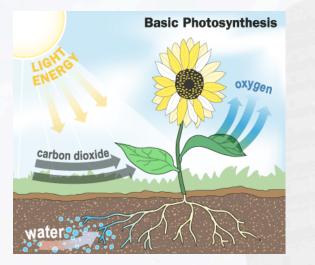
Provides the energy for most ecosystems on earth

Photosynthesis and Solar Energy

The Nobel Prize in Chemistry 1961



Joseph Priestley 1733–1804





M. Calvin 1911-1997

The Nobel Prize in Chemistry 1988



J. Deisenhofer

R. Huber



H. Michel

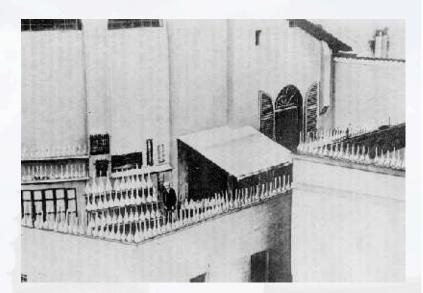


R. Marcus

The Nobel Prize in Chemistry 1992

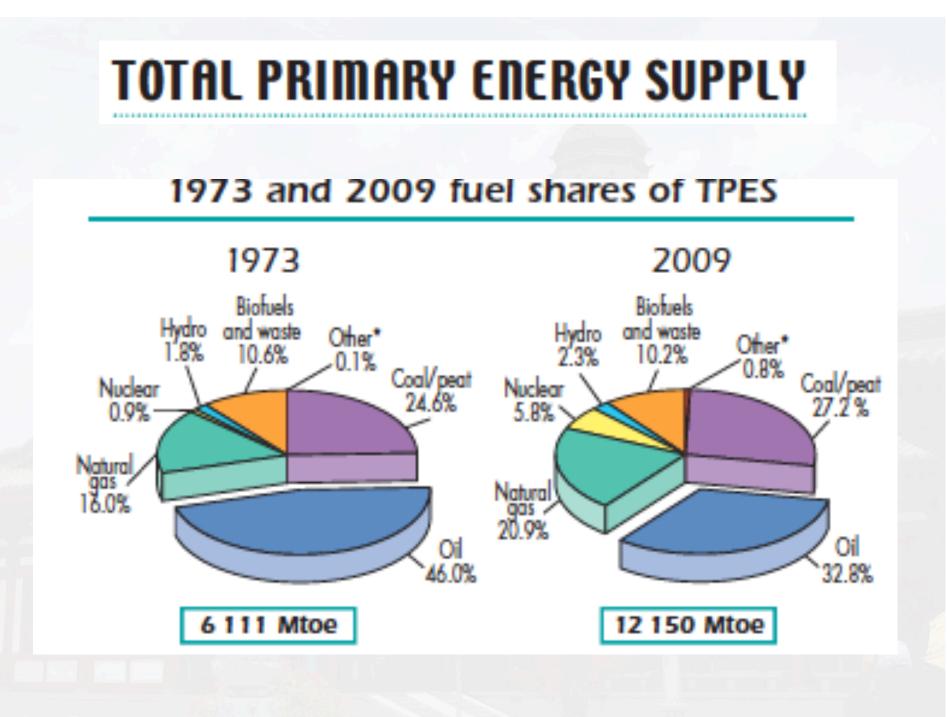


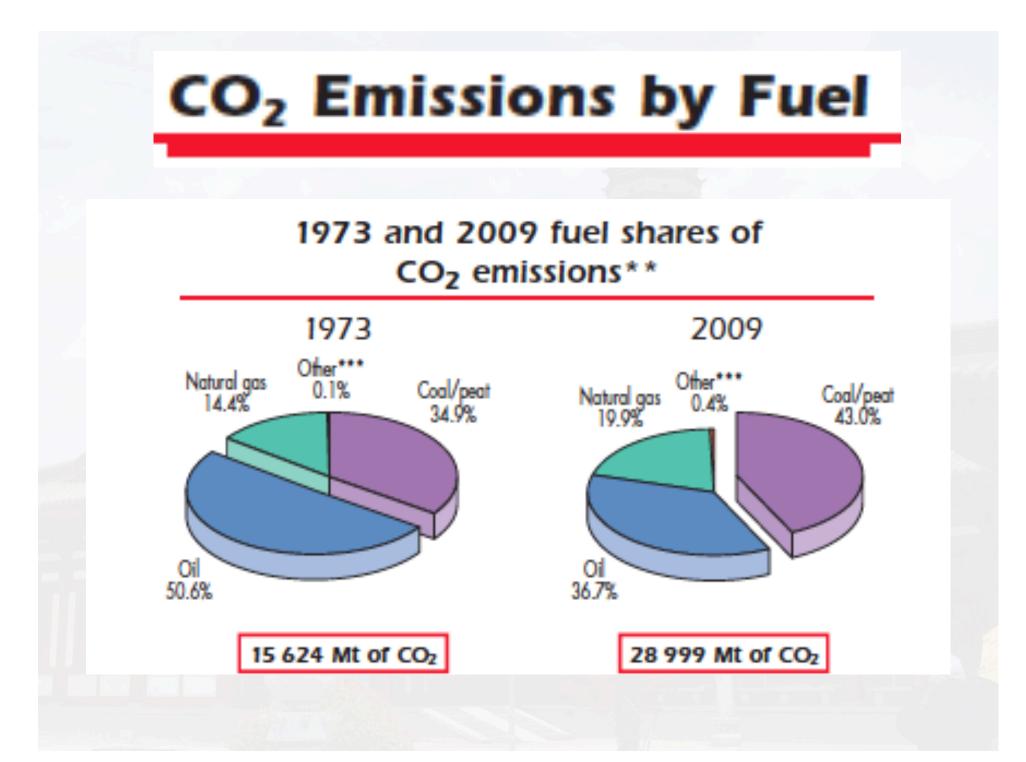
Giacomo Ciamician 1857-1922



"On the arid lands there will spring up industrial colonies without smoke and without smokestacks, forests of glass tubes will extend over the plains, and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is."

(Giacomo Ciamician Science 1912, 36, 385.)





We started using fossil fuels ambitiously around 1800. If we have a 500 year supply remaining.... And it took at least 70 million years to produce the fossil fuels we use today.... Once we use our 500 year supply, all we have to do is ... WAIT ANOTHER 70 MILLION YEARS !! tick, tick, tick Learn Photochemistry and Save the World



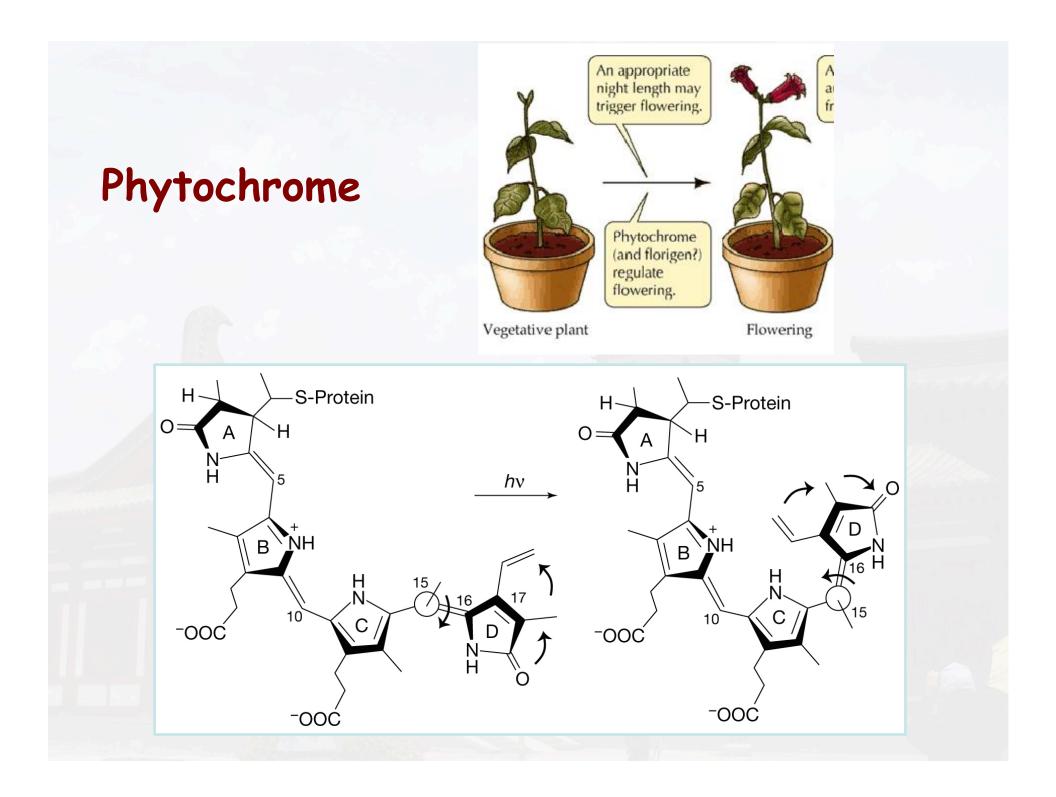
More optimism

"I have no doubt that we will be successful in harnessing the sun's energy. ... If sunbeams were weapons of war, we would have had solar energy centuries ago."

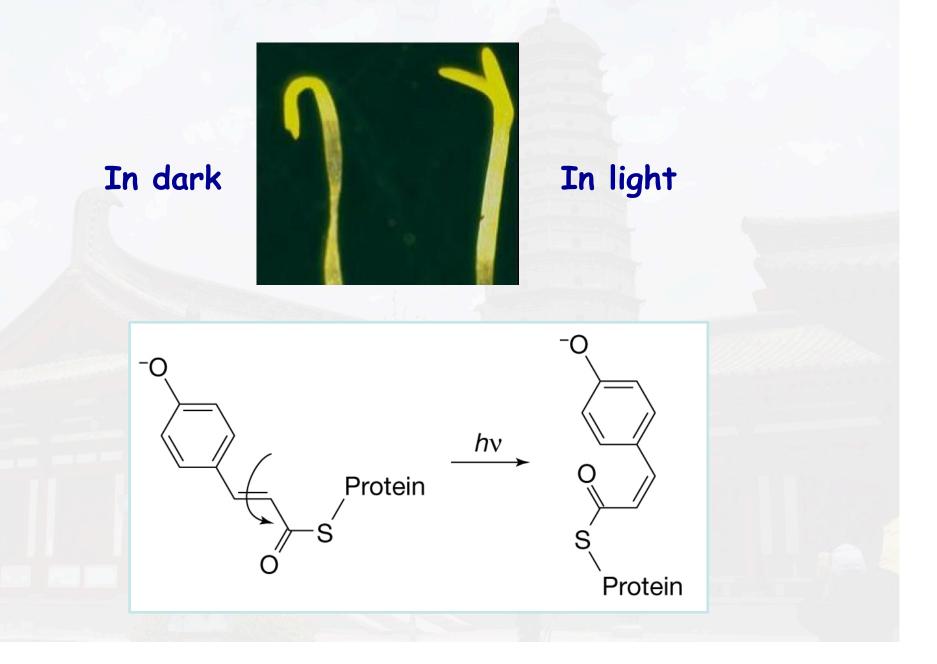


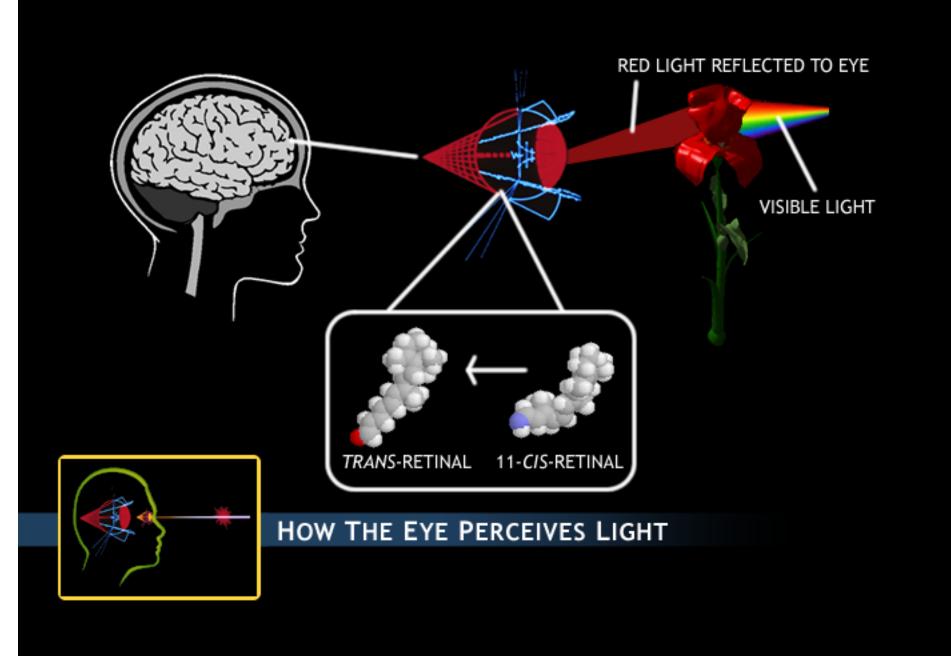
George Porter (1920 - 2002)

Observer, 1973



Role of Photoactive Yellow Protein (PYP) in plant growth

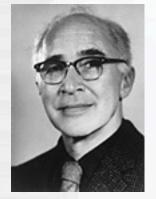




The Nobel Prize in Physiology or Medicine 1967





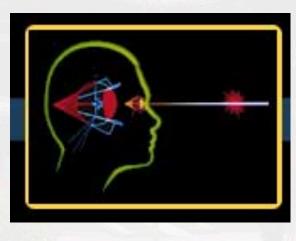


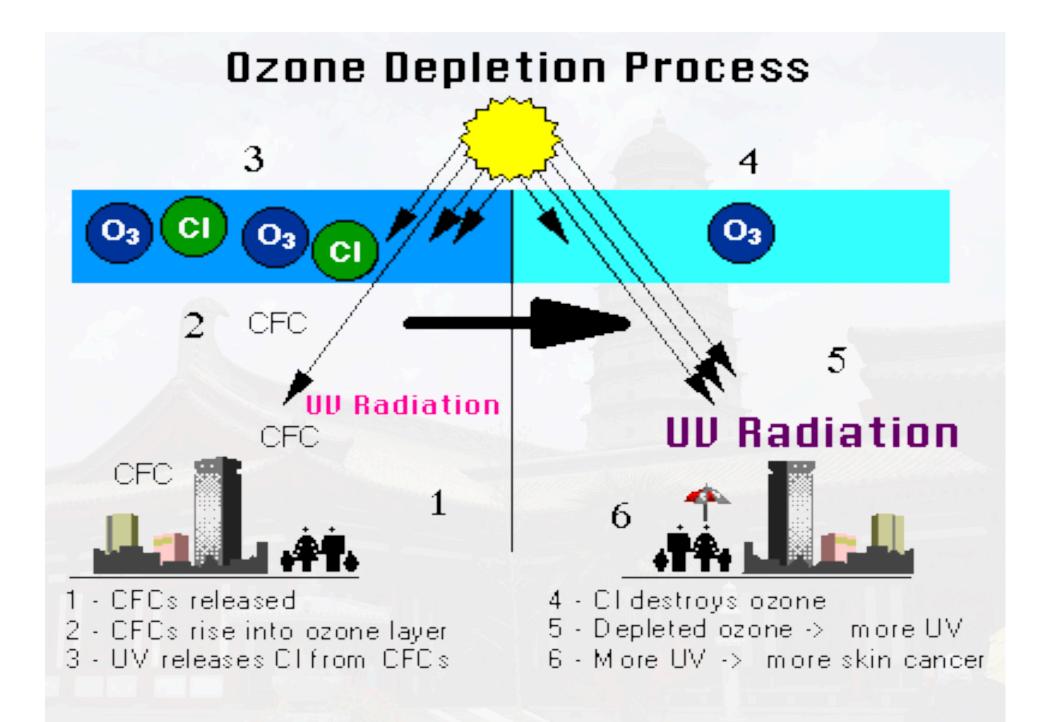
Ragnar Granit

Haldan Keffer Hartline

George Wald

"for their discoveries concerning the primary physiological and chemical visual processes in the eye"

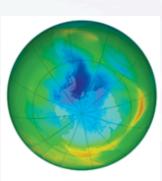




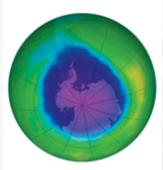
Ozone hole

 $O_2 \xrightarrow{h\nu} O + O$ $O + O_2 \xrightarrow{} O_3$ ozone

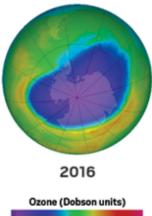
$$F \stackrel{Cl}{\longrightarrow} F \stackrel{Cl}{\longrightarrow} F \stackrel{Cl}{\longrightarrow} F \stackrel{I}{\longrightarrow} F$$



1979



1989



100 250 400 550

Paul J. Crutzen



The Nobel Prize in Chemistry 1995

Mario J. Molina



F. Sherwood Rowland

"for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone"

Our fore-fathers knew it, time for us to harness it



"The rising sun is the giver of energy, heat, all powers, happiness and prosperity." *Rigveda, 2000-1500 BC*