The world is our inspiration

Glycerol as a co-product of oleochemicals /biodiesel and vegetable oil derivatives from Castor oil for the production of fine chemicals in perfume and pharmaceuticals

Jean-Luc DUBOIS

Scientific Advisor, Directeur Scientifique

Catalysis and Processes

Part of the work presented here has been carried out within the Glyvalacr project sponsored by ADEME

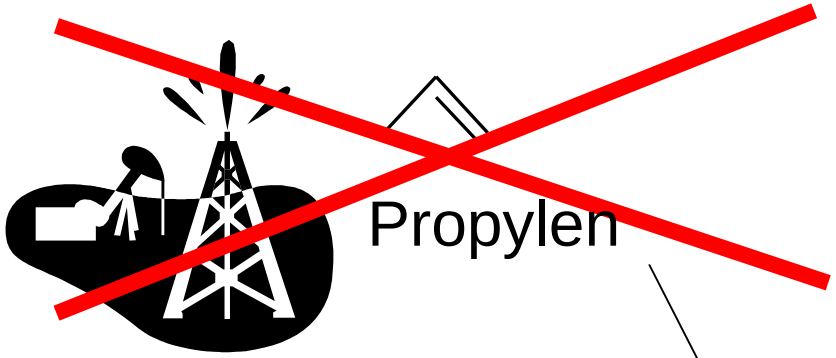
ARKEMA

The world is our inspiration

Arkema is a member of the European Biorefinery Projects

Acrolein and Acrylic Acid from Glycerol

Related to existing Network (steamcrakers, pipes)

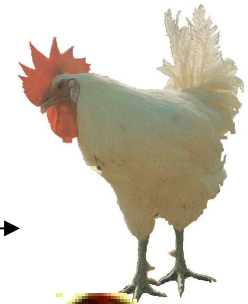


Propylen

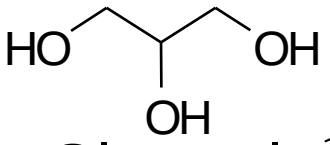
Acrolein derivatives

Fine Chemicals

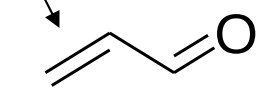
Methionine



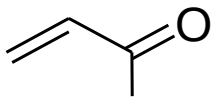
Ubiquitous



Glycerol



Acrolein



Acrylic Acid

Polyacrylics Dispersants for Pigments or $CaCO_3$

Esters

Fine Chemicals

Sources of Glycerin. (Worlwide).

10^3 Tons	2005	2006	2007	2008	2009
Soaps	160	150	155	130	110
Fatty Acids	410	450	470	470	490
Fatty Alcohols	130	160	180	190	200
Synthetic	20	-	-	-	-
Other	35	30	30	30	30
Biodiesel	368	550	635	853	1000
TOTAL	1123	1399	1470	1673	1830

Classical Acrolein and Acrylic acid processes

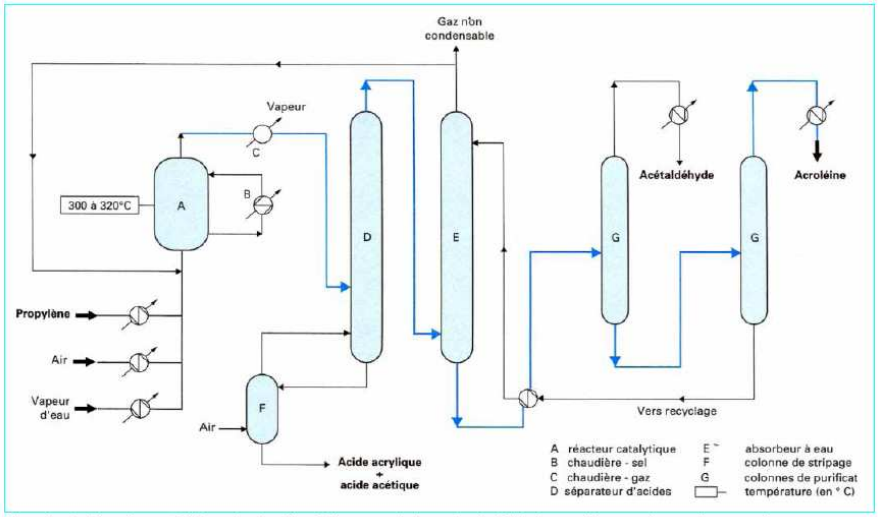


Figure 1 – Schéma d'une unité de production d'acroléine par oxydation ménagée à l'air du propylène, en présence de vapeur d'eau

Standard Acrolein plant:

- ➔Methionine: 30 kt/yr
- ➔Pyridine: few kt/tr
- ➔Glutaraldehyde: few kt/yr
- ➔Fine chemicals: few 100t/yr

Standard Acrylic Acid plant:

- ➔Superabsorbants,

Esters: 80 - 160 kt/yr

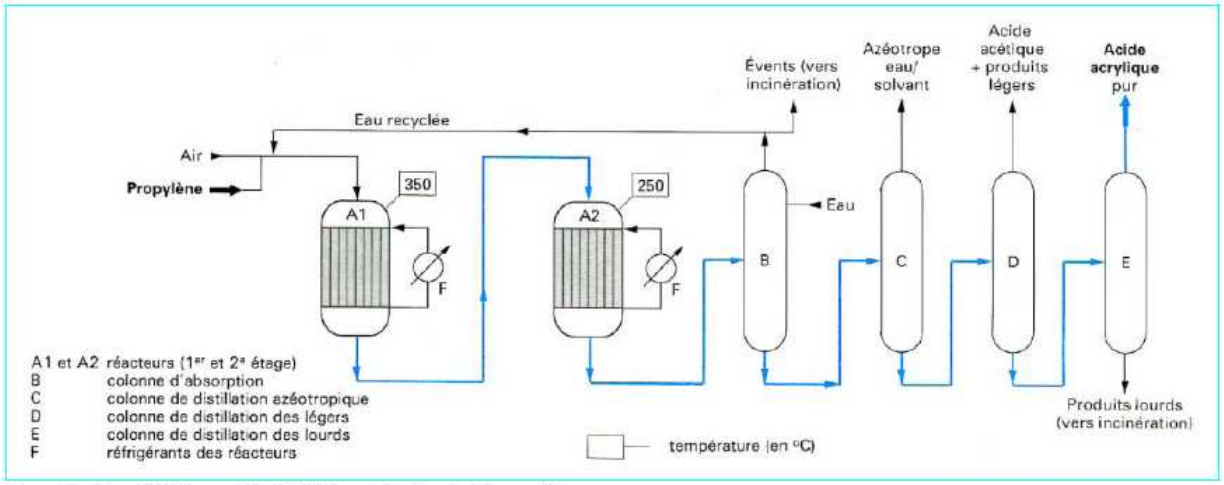
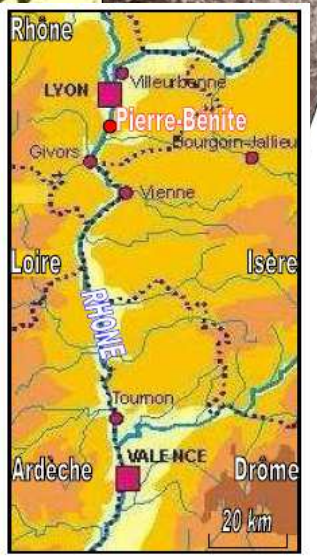


Figure 1 – Procédé Nippon Shokubaï de production d'acide acrylique

Techniques de l'ingénieur, 1995, J6055 and J6100

Environmentally Friendly Process: Avoid scenarios of past accidents

- Target: develop a new process for on-site Acrolein production (PROXI-plants) to avoid storage and transportation of a highly toxic Chemical.
- Pierre Bénite, France. July 10, 1976.
- Taft, USA/ December 10, 1982.



Major contamination of the Rhône River, during clean-up of a train tank
367 Tons dead fish

The Daily Record, Ellensburg, Wash., Sat., Dec. 11, 1982 Page 5

Explosion rocks Louisiana plant

TAFT, La. (UPI) — A fiery explosion of a storage tank at a chemical plant today shook south Louisiana's industrial corridor, forcing the evacuation of up to 25,000 people and the closing of the Mississippi River to ship traffic.

No injuries or deaths were reported in the explosion and resulting fire at the Union Carbide plant. Company officials said the storage tank was surrounded by protective mounds of dirt.

"The immediate concern is the adjacent tanks that have additional explosion potential," Union Carbide spokesman Jim Tate said from a concrete command post on the plant grounds.

"As a precautionary measure and to the minimize the risk to the surrounding areas, an evacuation has been conducted by the state police."

Civil Defense officials said as many as 25,000 people had been forced from their homes.

The Coast Guard said it closed the river to ship traffic, describing the move as a precaution against Acrolein fumes, although no immediate danger was reported. The chemical is a yellowish or colorless pungent liquid sometimes used for the production of tear gas.

17,000 Louisiana Residents Return Home as Site of Blast Is Declared Safe Aerial view of the wreckage of tanks after an explosion and fire Saturday at the Union Carbide chemical plant in Taft, La. Residents within a five-mile radius of the site were evacuated because of the fear of toxic fumes from the fire. They were permitted to return home yes-terday. River traffic near the plant, situated on the banks of the Mississippi River 30 miles west of New Orleans, was halted until fire burned itself out. The chemical in the tanks was acrolein, which is used to make algaecides, animal food supplements and tear gas.

The New York Times

Explosion of a Storage facility
17000 people evacuated

Cradle to gate analysis

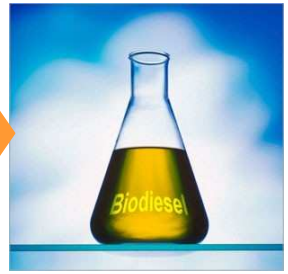
CO_2

Plant growth = consumption of atmospheric CO_2

- **Acrolein ex propylene: 3190 kg CO_2/t**
- **Acrol. ex glycerol: Target 980 kg/t**
- **Acrylic acid ex Propylene: 950 kg CO_2 /t**
- **Acrylic Ac. ex glycerol: target 0 kg/t**

Vegetable Oil

Methanol Transesterification



Biodiesel

Diesel Blend

Glycerine

Acrolein/
Acrylic Acid

ADEME

Done within the Glyvalacr Project sponsored by Ademe

ARKEMA
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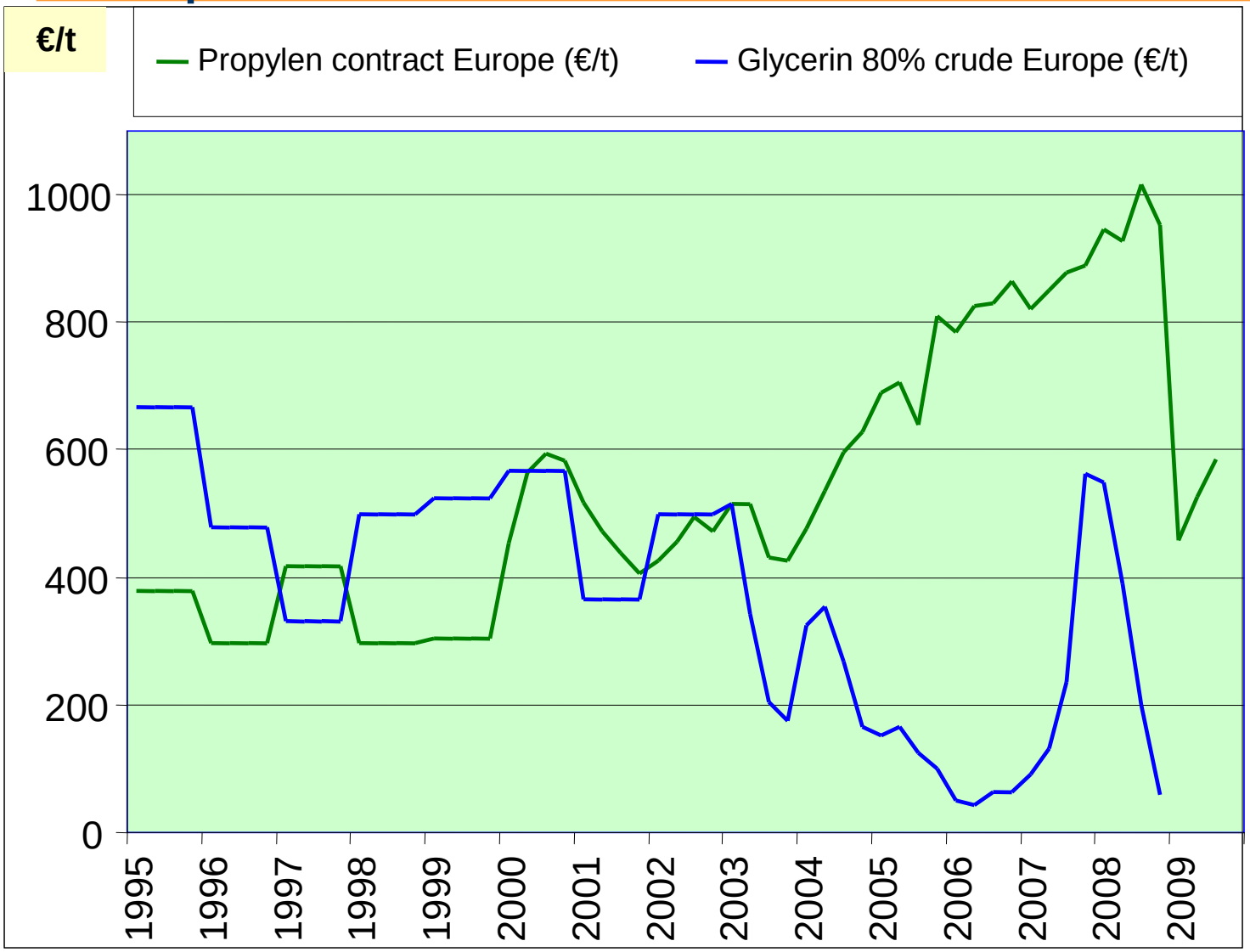
Historical prices: propylene and glycerol in Europe

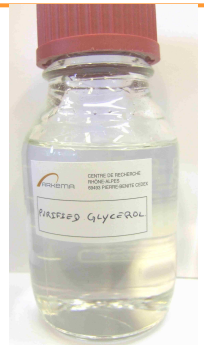


- Glycerol and Propylene historical prices; drivers are not the same

Basic Design of Industrial Plant

Glycerol

Storage



Glycerol phase

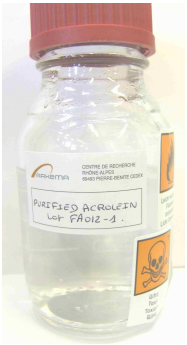
Acrolein or acrylic unit

reaction + purification

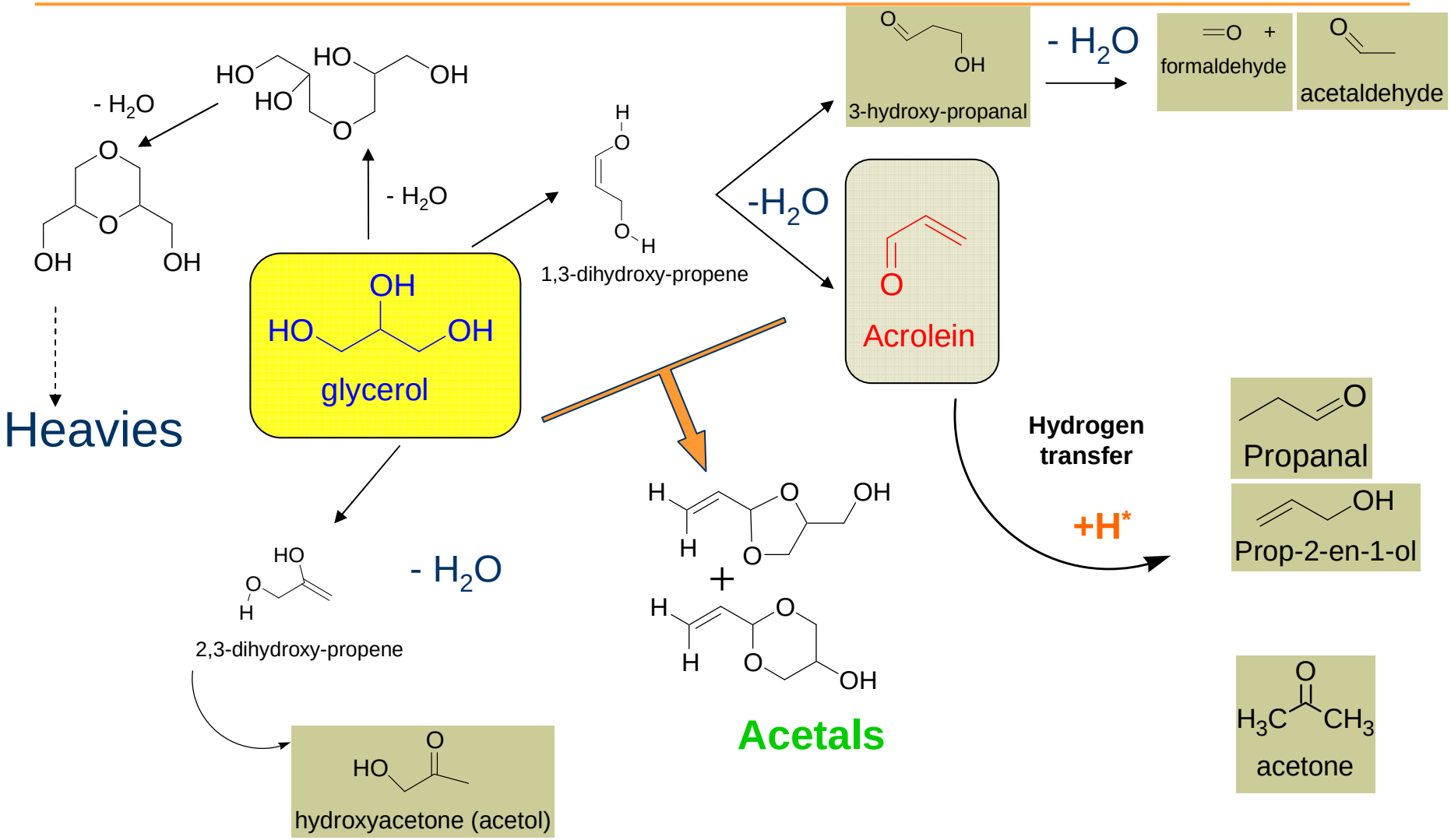
Thermal Oxidizer

Separation unit

Acrolein or Acrylic Acid storage



Reaction mechanism



Glycerol to Acrolein- Operating conditions (Typical)

- Operating Conditions.
  - Temperature: 300-320℃
  - Pressure: 2 bara
  - GHSV: 2 250 Hr-1
- Catalyst: WO_3/ZrO_2 (solid acid)
- Ratio Glycerol/Water: 30/70 (w./w.)
- Ratio O_2/Glycerol: 0.42 (mole/mole)
  - Glycerol: 6.7 % vol.
  - Water: 79.9 % vol.
  - O_2: 2.8 % vol.
  - N_2: 10.6 % vol.

Acrolein purification
Example of product qualities

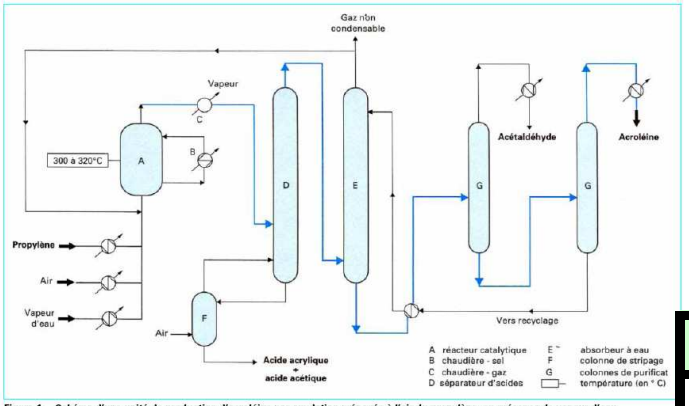


Figure 1 – Schéma d'une unité de production d'acroléine par oxydation ménagée à l'air du propylène, en présence de vapeur d'eau

	Reference	Reference	Reference
	12931	13948-crude	13948-purif
	wt %	**wt %**	**wt %**
H2O	3.24	4.16	3.00
Acetone		0.22%	0.34%
2,3-butanedione		0.11%	0.08%
Propionaldehyde	1.18%	0.75%	0.55%
Hydroxypropionaldehyde	0.05%	0.00%	0.00%
Formaldehyde	0.065%	0.154%	0.049%
Acetaldehyde	10.5%	12.2%	0.74%
2-oxopropanal		0.0496%	0.0201%
Crotonaldehyde		0.0998%	0.0240%
Acrolein dimer		0.0019%	0.0011%
HydroQuinone (stabilizer)	0.2165%	0.1879%	0.1325%

12 Principles of Green Chemistry

1. Prevent waste ➔ We use a waste
2. Design safer Chemicals and Products ➔ Same products offer market access
3. Design less hasardous chemical synthesis ➔ Process for on-site production
4. Use Renewable feedstocks ➔ Glycerol
5. Use catalysts not stoichiometric reagents ➔Heterogeneous Catalyst
6. Avoid Chemical derivatives ➔ Direct route
7. Maximize atom economy ➔ C3 to C3
8. Use safer solvents and reaction conditions ➔ no solvent, safer process
9. Increase Energy effciency ➔ Translated into CO_2 balance
10. Design Chemicals and products to degrade after use ➔ return plant-based CO_2 to the atmosphere
11. Analyse in Real time to prevent pollution ➔ Target = on-time consumption
12. Minimize the potential for accidents ➔ Avoid transportation and storage

Industrial property : Arkema portfolio

- **5 granted patents**

  - EP1,848,681B1 US7,655,818
    WO06/087084 (02/05) Glycerol→Acrolein with highly acid solid catalysts (H_0 -18 to -9)

  - US7,396,962 WO06/087083 (02/05) Glycerol→Acrolein in the presence of O_2

  - US7,531,699 WO07/090990 (02/06) Glycerol + propylene → acrolein

  - EP1,981,835B1, US7,880,034
    WO07/090991 (02/06) Glycerol + propylene → acrolein → acrylic acid

  - US7,910,771 WO06/114506 (04/05)
    Glycerol → Acrolein → acrylic acid in the presence of O_2 in a single reactor

And much more in a near future…

Industrial property : Arkema portfolio

32 published patent applications

- WO08/007002 (07/06) Glycerol → acrylic acid with 2-layered catalyst (not extended)
- WO08/087315 (12/06) Glycerol → acrylic acid with intermediate condensation of water after dehydration step
- WO08/129208 (03/07) Vaporisation/purification of glycerol in fluidized bed
- WO09/044051 (09/07) Reactive vaporisation of glycerol in fluidized bed
- WO09/044081 (09/07) Glycerol→Acrolein with modified iron phosphate catalysts
- WO09/081021 (12/07) Glycerol→Acrolein through acetals from glycerol + acrolein
- WO09/136537 (04/08) Catalyst made of salt of heteropolyacid for glycerol→Acrolein (with NK)
- WO09/127889 WO09/128555 (04/08) Glycerol→Acrolein with salt of heteropolyacid
- WO09/156664 (06/08) Use of acidic gas in glycerol dehydration
- WO10/10291 WO10/10298 (07/08) Propionic acid and vinyl propionate from cristallisation of glycerol-based acrylic acid
- WO10/031649 (09/08) Process for biobased glacial acryclic acid
- WO10/047905 (10/08) VPO catalyst for glycerol→Acrolein (with NK)
- WO10/046227 (10/08) Glycerol→Acrolein with VPO catalyst
- WO11/010035 (07/09) Process for glycerol based acrylic acid that comprises an azeotropic drying step and a crystallisation step
- WO11/010036 (07/09) Process for glycerol based acrylic acid that comprises an absorption with hydrophobic solvant and a crystallisation

Industrial property : Arkema portfolio

32 published patent applications

- WO11/033689 (09/09) Catalyst & process: glycerol → acrolein with metal supported on TiO_2
- WO11/046232 (09/09) Catalyst & process glycerol → acrolein with salt of heteropolyacid supported on a support.
- WO11/073552 (12/09) Acrolein & acrylic acid process from glycerol with elimination of impurities in a water loop by oxidation
- FR2953830(12/09) Acrolein & acrylic acid process from glycerol with elimination of impurities in a water loop or by evaporation or condensation

- WO08/113927 (02/07) Glycerol → Acrolein → acrylonitrile
- **WO09/153529 (06/08) Biosourced acrolein polymer**
- WO10/010309 (07/08) Acrylate esters from glycerol
- WO10/058129 (11/08) Methylmercaptopropionaldehyde and methionine from glycerol
- FR 2,939,055 (12/08) Dispersing or grinding agent from glycerol-based acrylic acid (Coatex)
- WO10/106267 (03/09) Bio-based impact modifier
- FR 2,943,351 (03/09) Bio-based acrylic processing aid
- WO10125276 (04/09) Technical biobased acrylic acid → acrylate ester → Acrylate polymers
- WO10/130919 (05/09) Bio-based acrylic wood adhesive
- **WO11/055051(11/09) Biobased glutaraldehyde**
- **WO11/055057(11/09) Biobased pyridine and picoline**

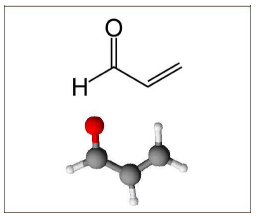
And much more in a near future…

Further applications of a Glycerol to acrolein technology

- Fine Chemicals (perfumes/pharmaceuticals)
- Antimicrobial polymer
- Acrylic acid
- Acrylonitrile
- Acrylamide
- Glutaraldehyde
- Pyridine
- …

Acrolein

- Melting point: -88 ℃
- Boiling point:
  - 53 ℃ @ 760 mmHg
  - -11 ℃ @ 50 mmHg
  - -36 ℃ @ 10 mmHg
- Solubility:
  - 20 g/100 ml water @ 20 ℃
  - 6.8 g water / 100 g solution @ 20 ℃
- Density: 0.84
- Self ignition temperature:
  - 234 ℃
- Flash point: -26℃ cc
- Flammability limits in Air:
  - 2.8 – 31 %
- Vapor pressure:
  - 29 kPa @ 20 ℃
- VLE: 0.25 mg/m^3
- LD50:
  - (rat): 46 mg/kg
  - (mouse): 40 mg/kg



Phrases R : 11,24/25,26,34,50,

Phrases S : 23,26,28,36/37/39,45,61,

SGH[5]

Danger

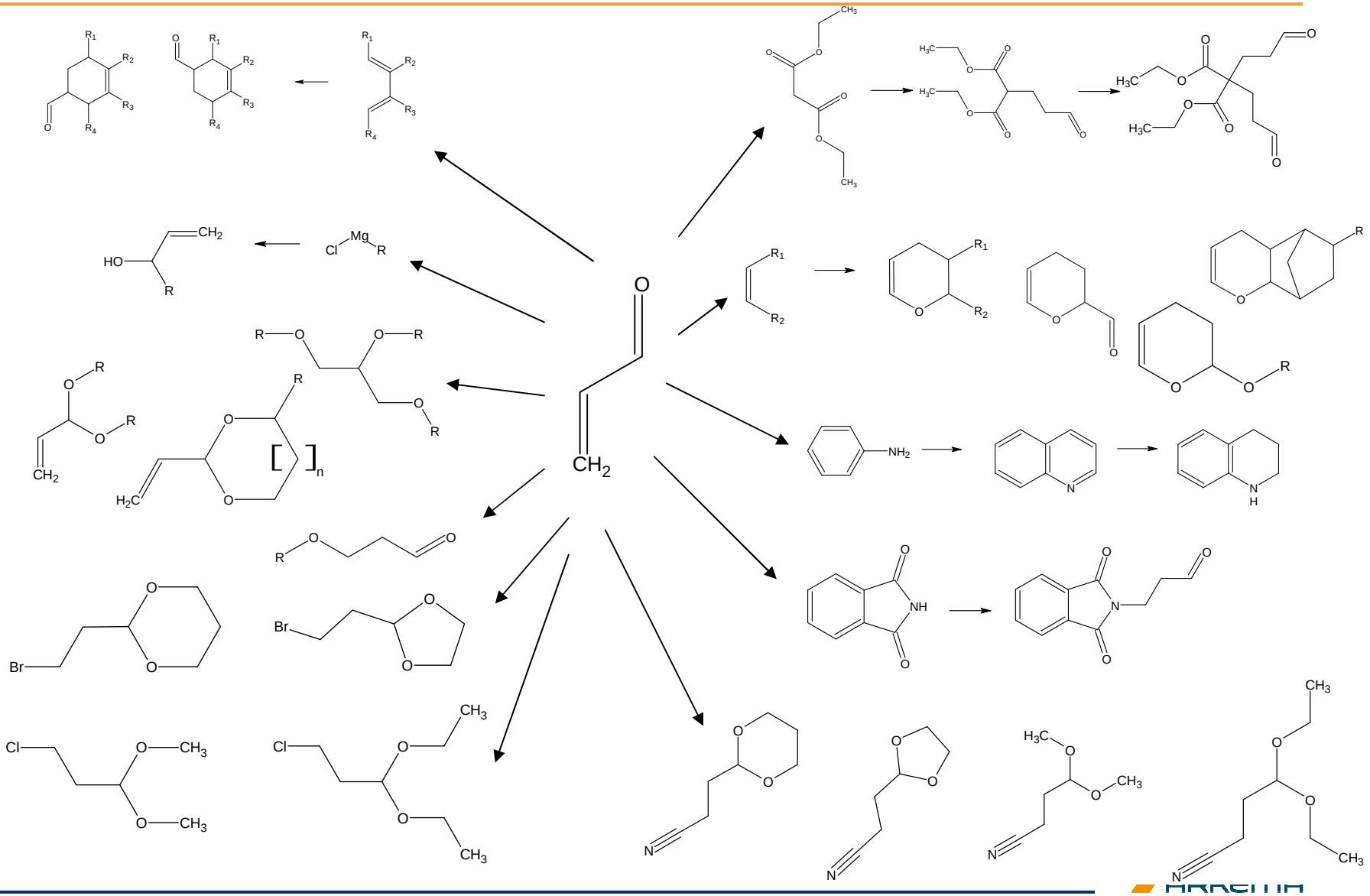
H225, H301, H311, H314, H330, H400,

N° CAS	107-02-8 [1]
N° EINECS	203-453-4 [2]

The world is our inspiration

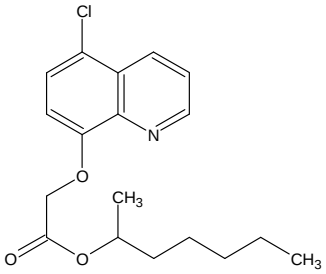
Acrolein Uses

Acrolein: a platform molecule, for Bio-based products

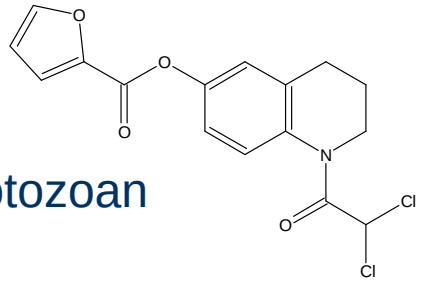


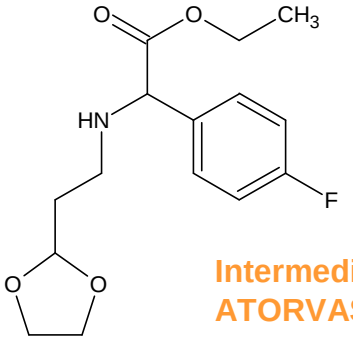
Some products made out of Acrolein

Cloquintocet-M
Ciba Geigy's herbicide



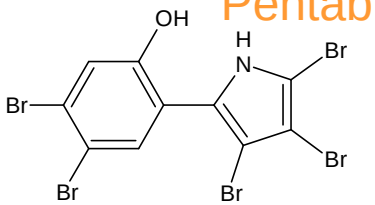
Quinfamide
Winthrop antiprotozoan

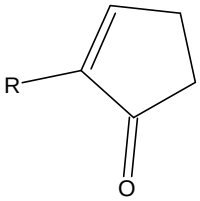




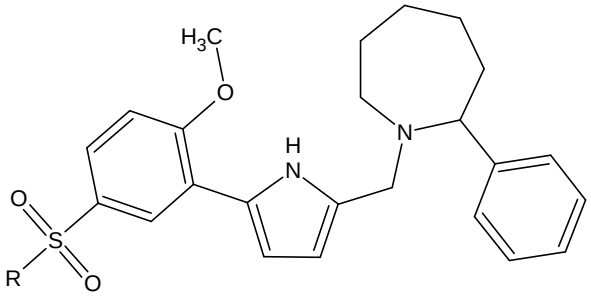
Intermediate to ATORVASTATIN

Pentabromopseulidin

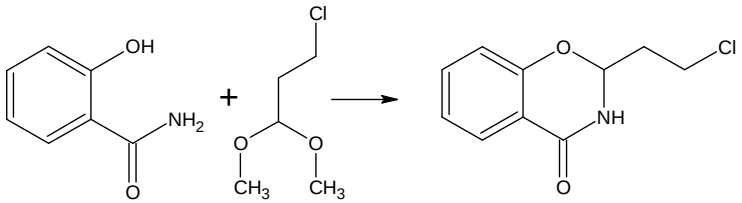




Cyclopentenone
(used in Jasmone industry)

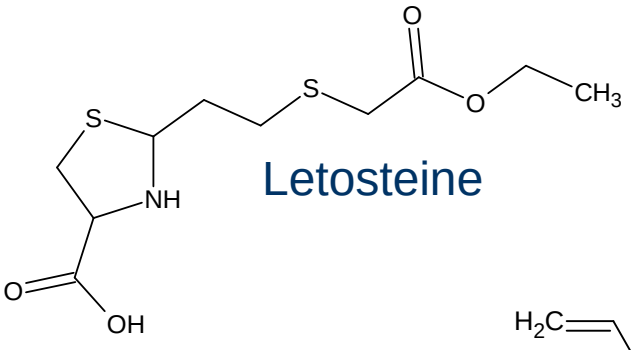


Dopaminergic

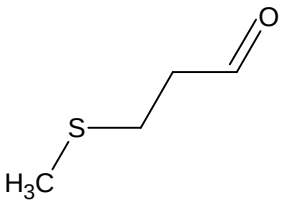


Chlothenoxazine
(analgesic)

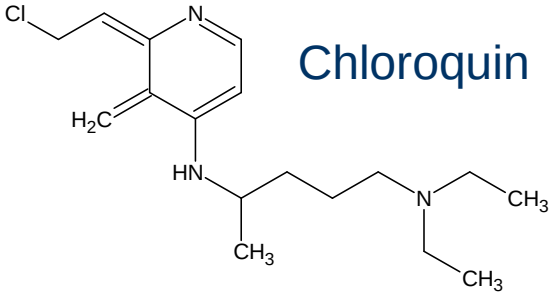
Some other products made from Acrolein



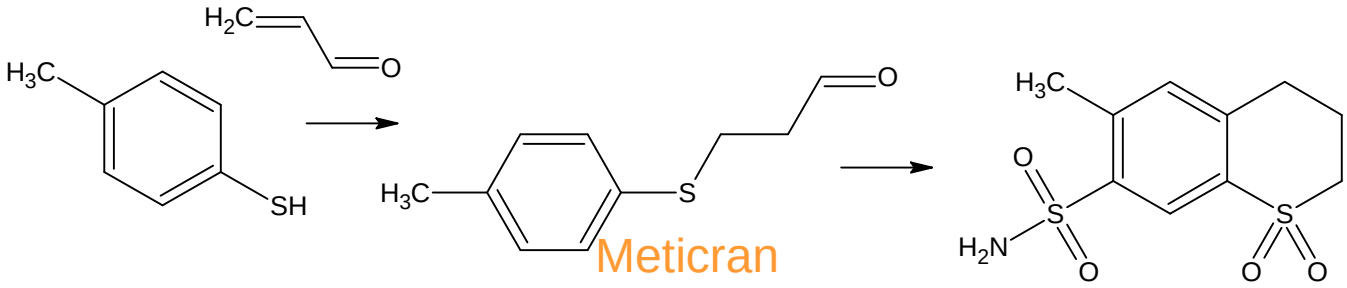
Letosteine



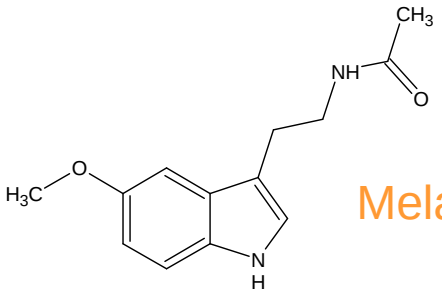
Methional → Methionine



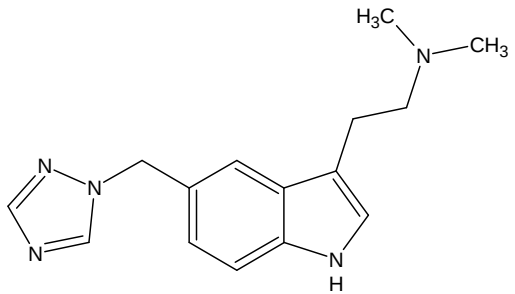
Chloroquin



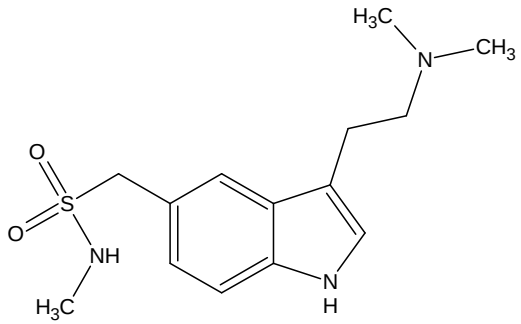
Meticran (diuretic)



Melatonin

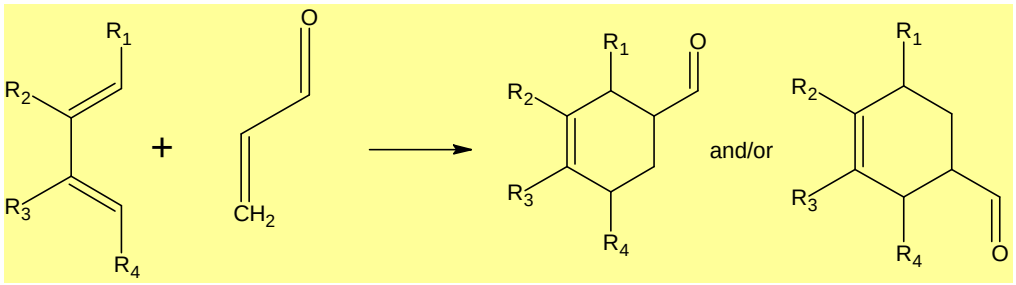


Sumatriptan

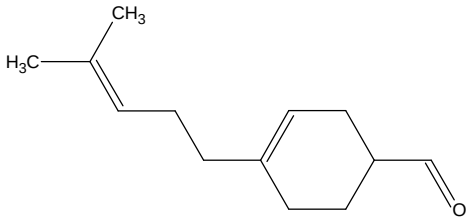


Rizatriptan

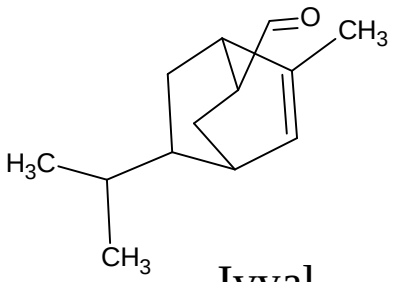
Diels Alder Reactions



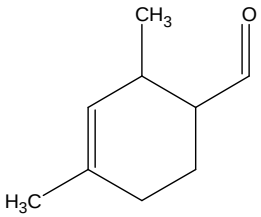
Perfumes/ Fragances



Muguet Aldehyde

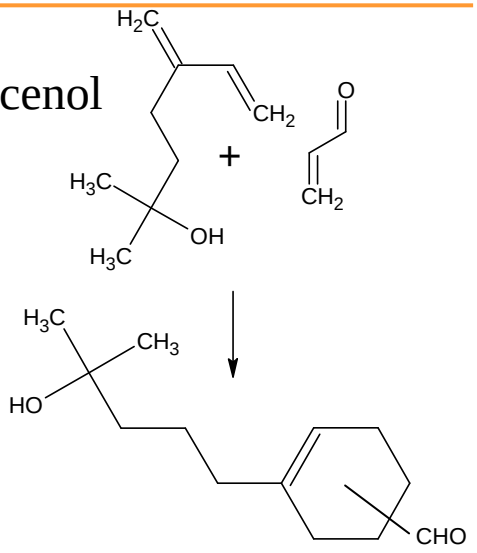


Ivyal



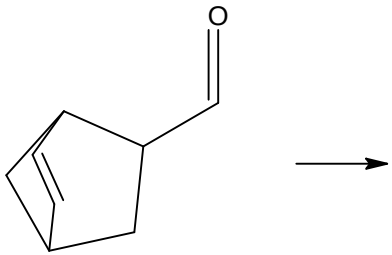
Trivertal

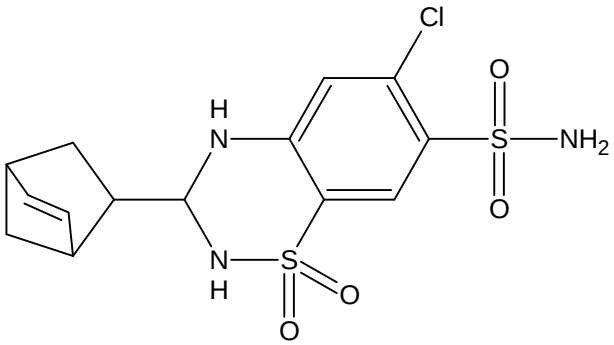
Myrcenol



Lyral

Pharmaceutical

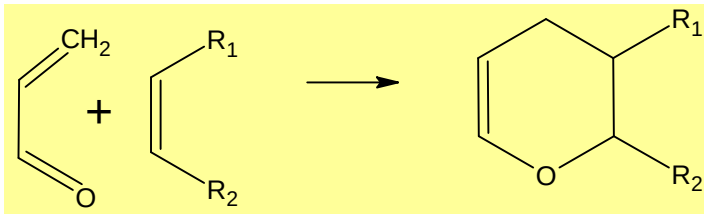




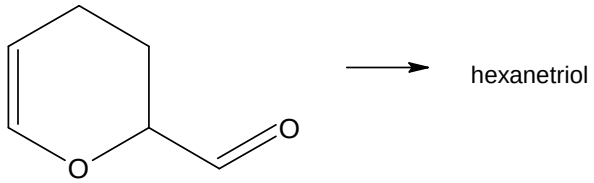
Norbornene carboxaldehyde

Cyclothiazide (diuretic)

Diels-Alder (Acrolein as 1,3 diene)

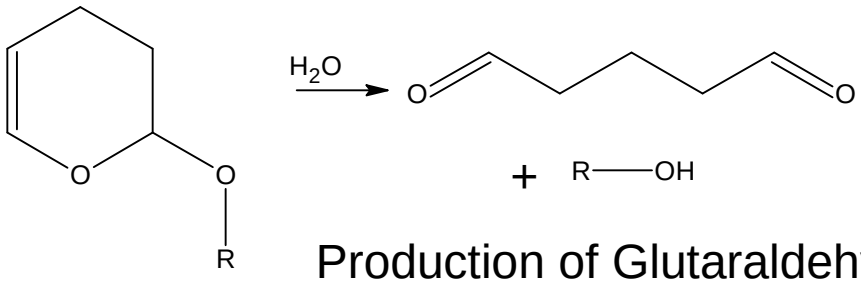


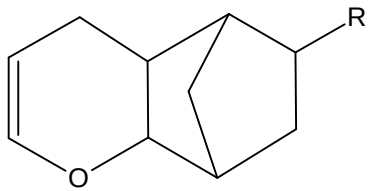
Acrolein dimer



3-Cyclohexene-1-carbaldehyde, forms a cyclic acetal with pentaerythritol, used as stabilizer against ozone in rubber.
Also used for the synthesis of cycloaliphatic epoxides

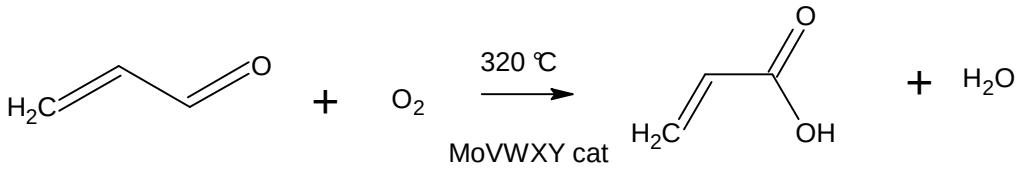
Hetero Diels-Alder



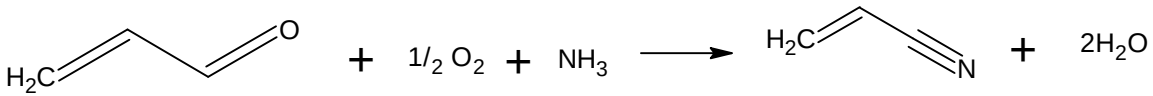


Production of Glutaraldehyde

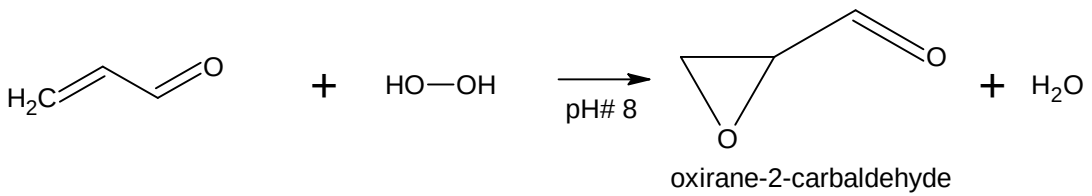
Oxidation / Ammoxidation



Acrylic Acid

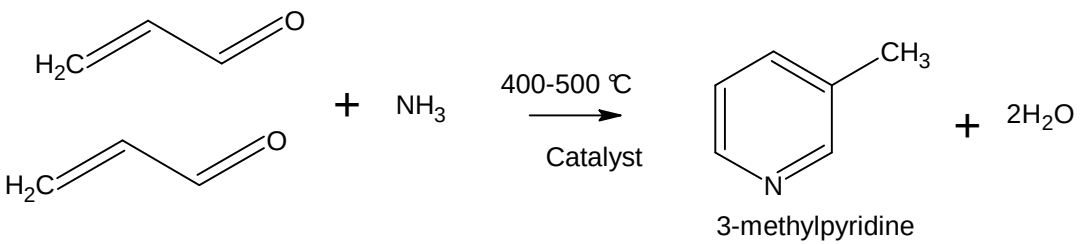


Acrylonitrile



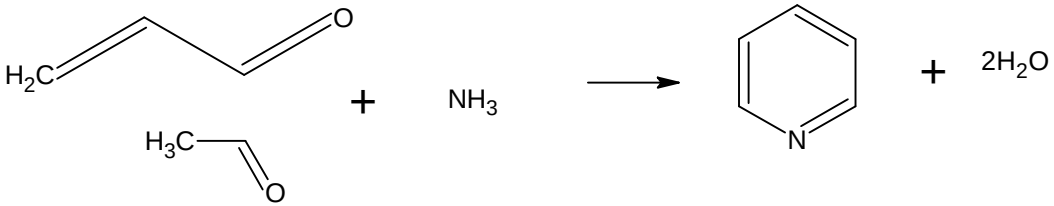
Glycidaldehyde

Pyridine derivatives

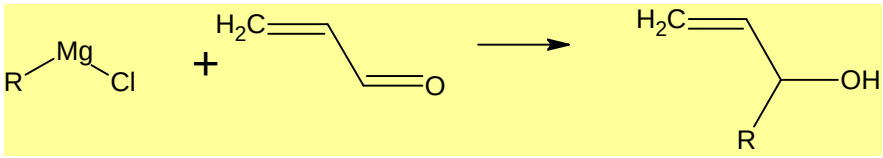


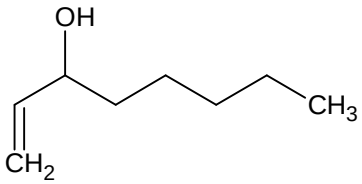
3-methylpyridine

Intermediate to nicotinic acid (niacin)

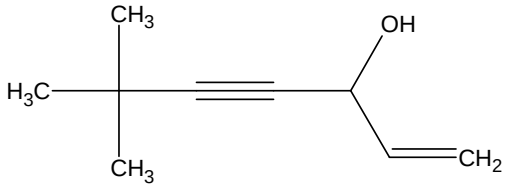


Vinyl alcohols through Grignard reactions

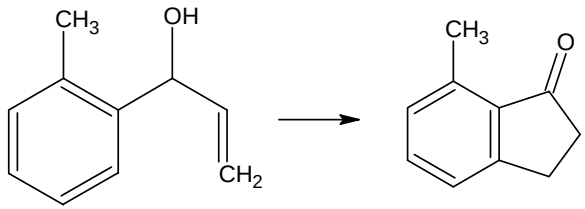




Octene-1-ol-3

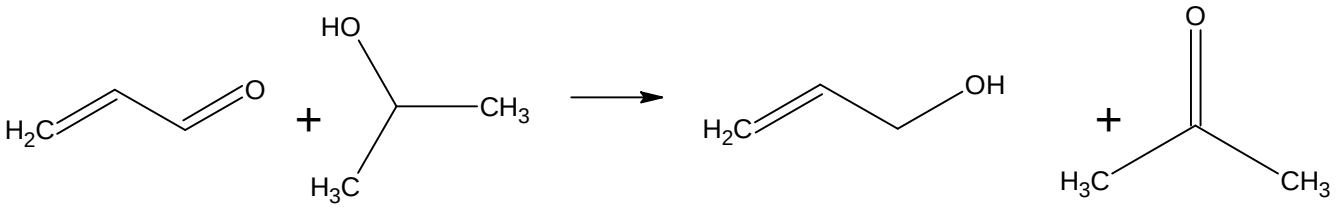


Indanone precursors

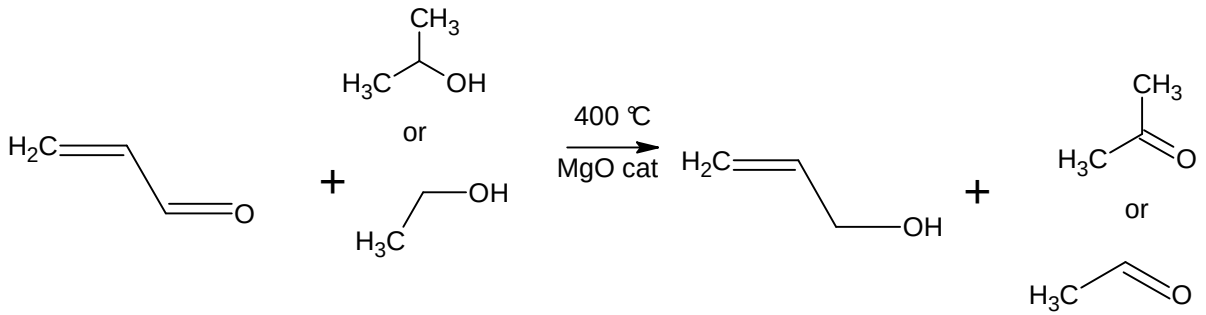


Terbinafin side chain

Vinyl Alcohol through reduction



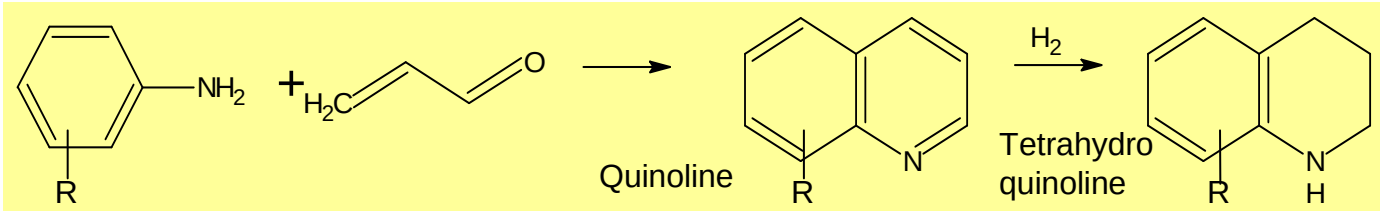
Hydrogen transfer reaction (Meerwein-Ponndorf), in liquid phase



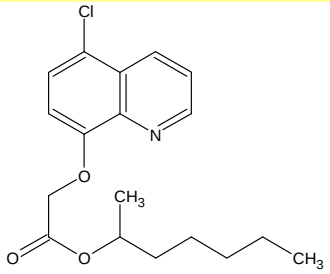
Gas phase reaction

Amine derivatives

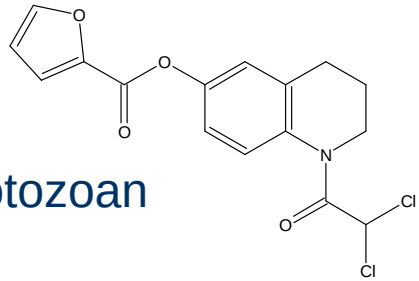
(Skraup Reaction)

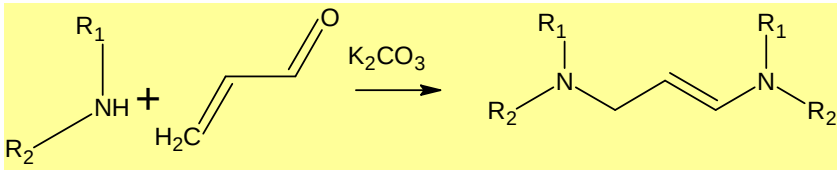


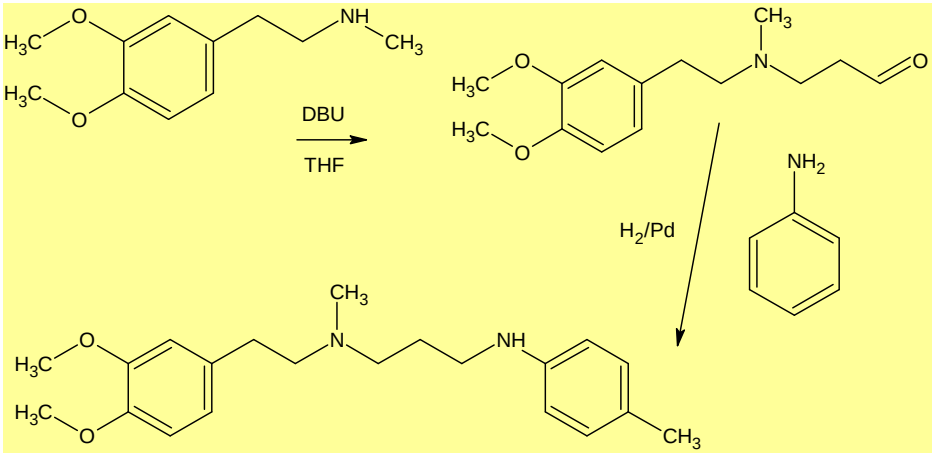
Cloquintocet-M
Ciba Geigy's herbicide



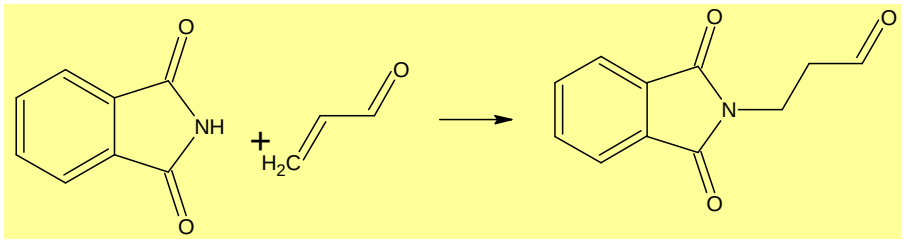
Quinfamide
Winthrop antiprotozoan



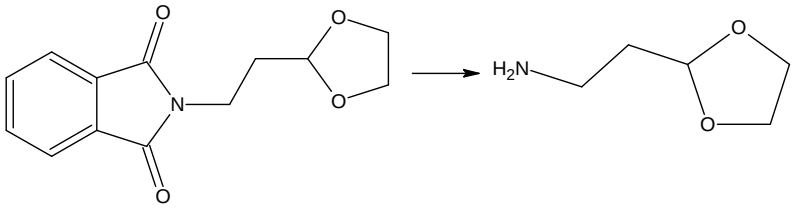




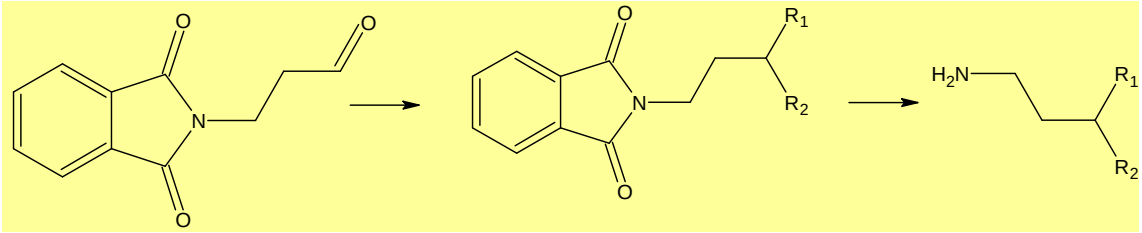
Phthalimido compounds



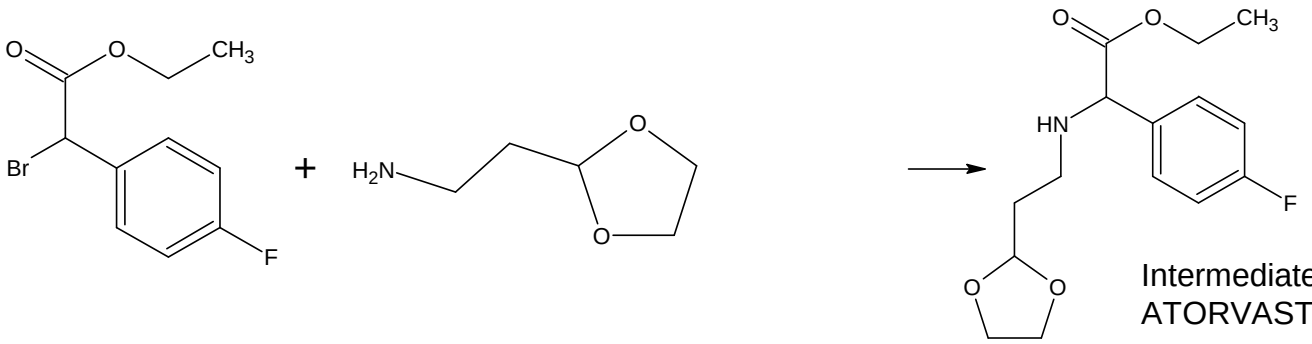
Phthalimido propanal



Ethylene acetal amino propionaldehyde



3-aminopropanes

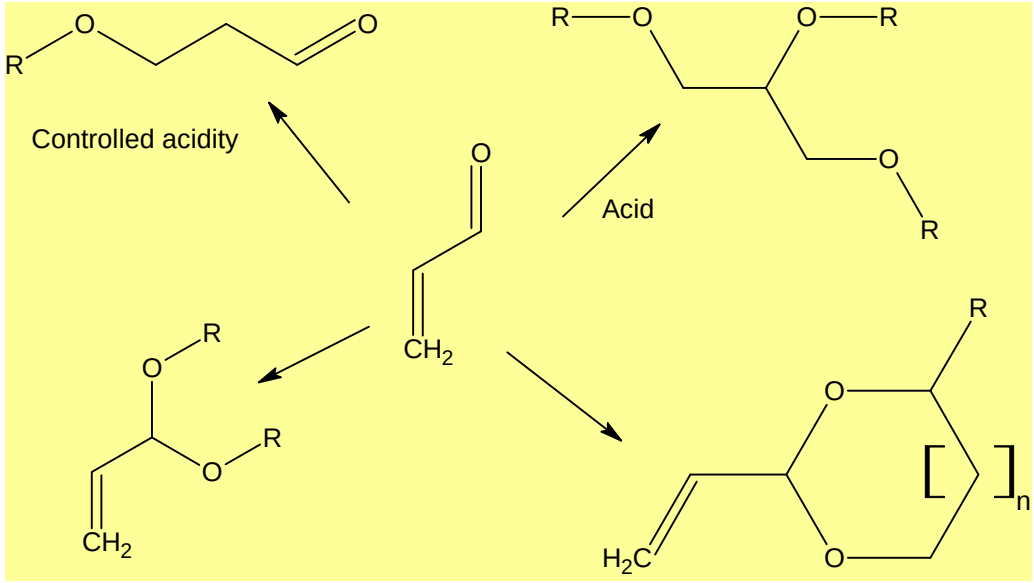


Intermediate to
ATORVASTATIN

Acrolein and alcohols

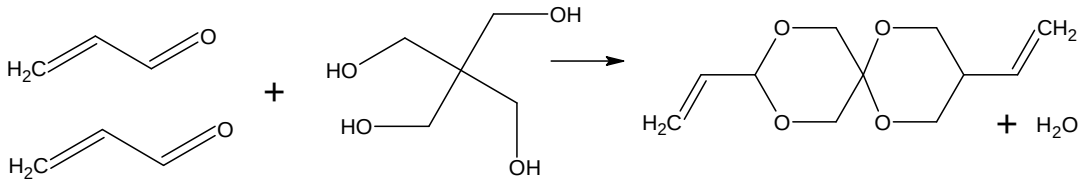
3-alkoxypropanal

Trialkoxypropane

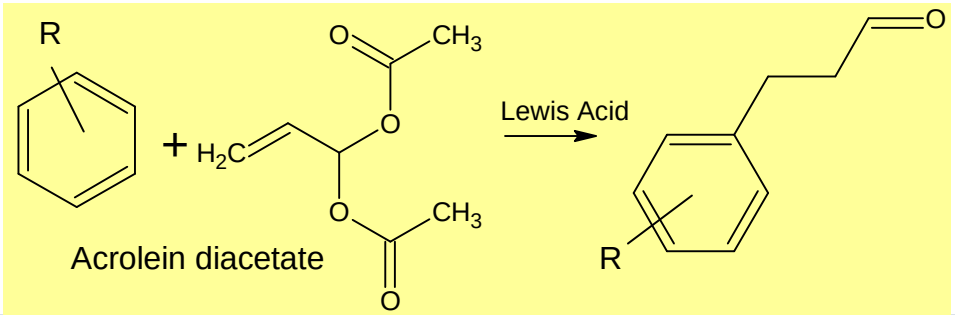


Acetal
(high yields when combined with extraction)

Vinyl dioxan & dioxolan
(more easy to form)



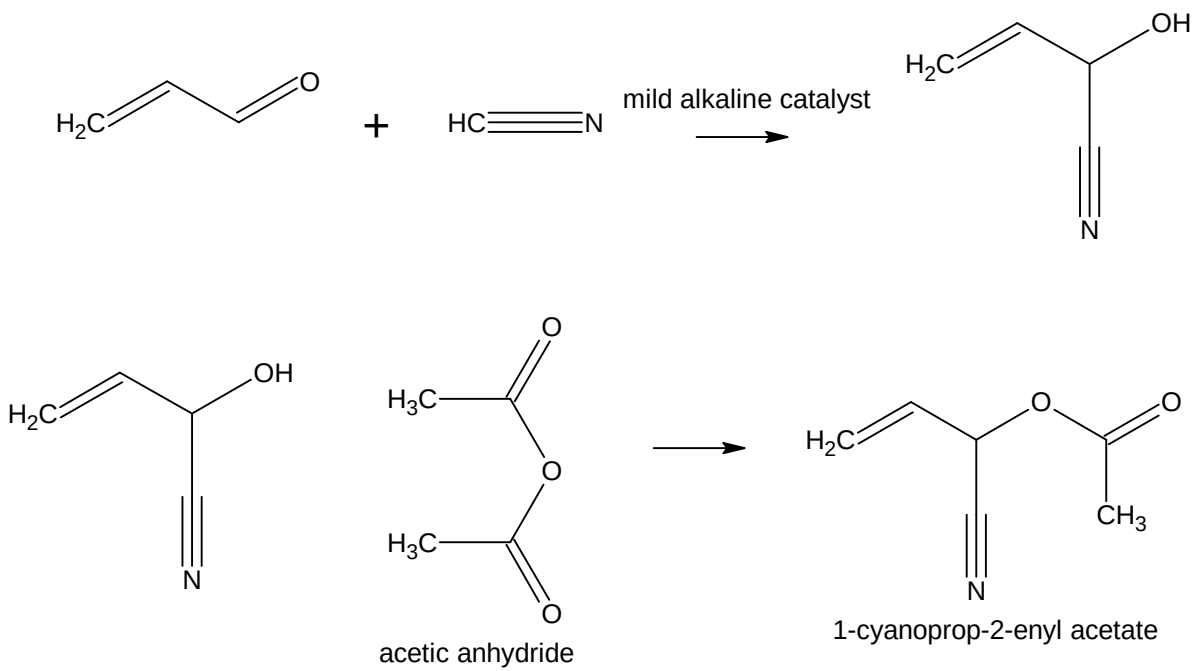
Monomer for spirane resins



3-phenylpropanal

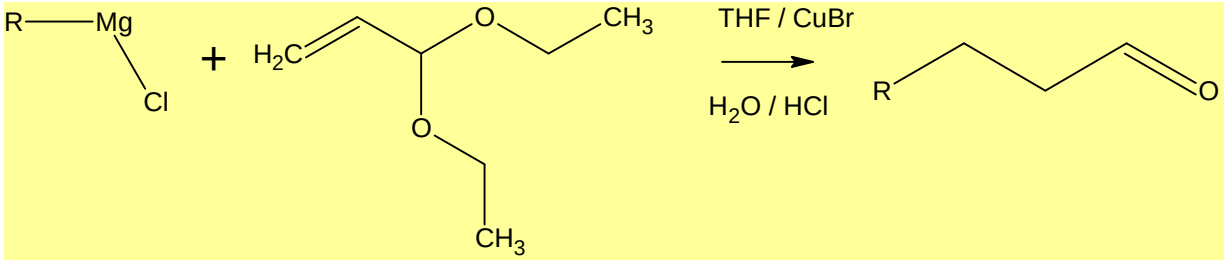
Acrolein acetate is obtained by acid catalyzed reaction of acrolein and acetic anhydride

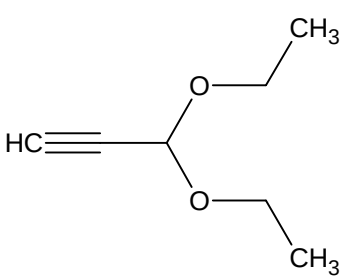
Reaction with HCN

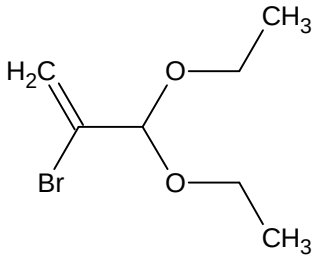


Intermediate for pharmaceutically and biologically active substances

Propargyl







Propargyl aldehyde
DEA

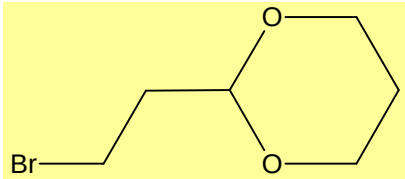
Pyroles

2-Bromo diethoxypropene

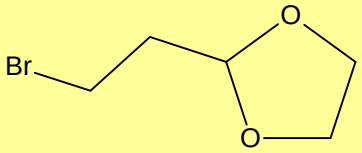
2-methylene cyclopentanone

Halogen Propionaldehyde Acetals Building blocks (acetals react with HX)

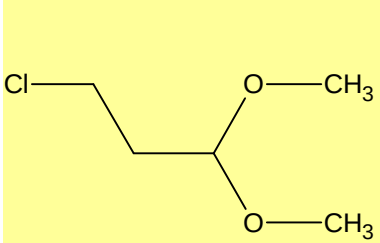
BED
(dioxan)



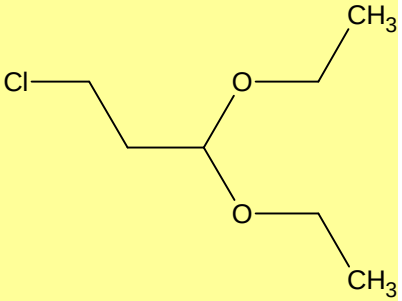
BEDO
(dioxolan)

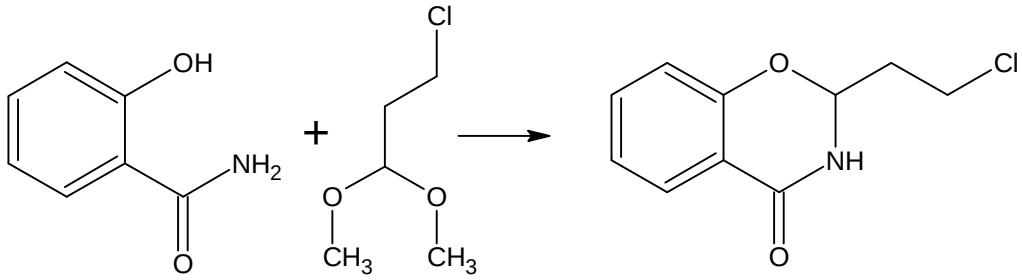


CPDMA

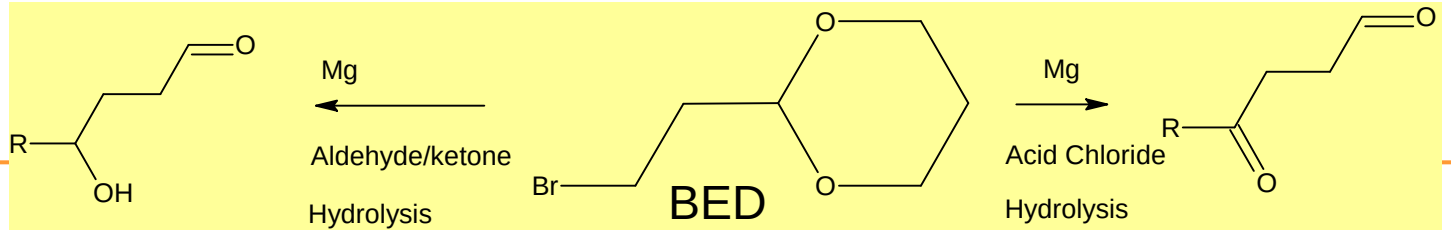


CPDEA



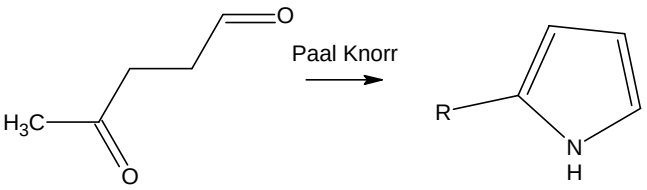


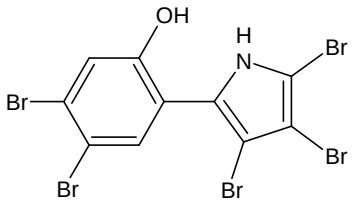
Chlothenoxazine
(analgesic)



4-hydroxybutyraldehydes

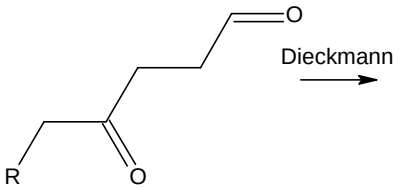
4-oxobutyraldehydes

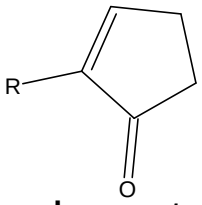




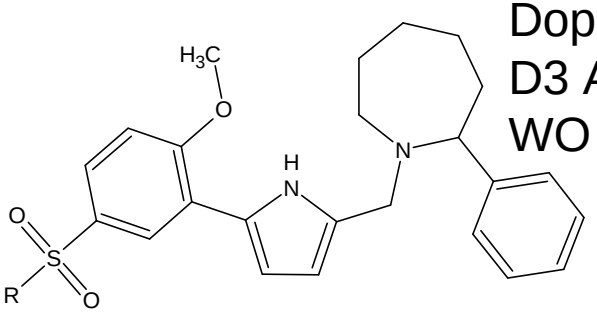
Pentabromopseulidin

Pyroles

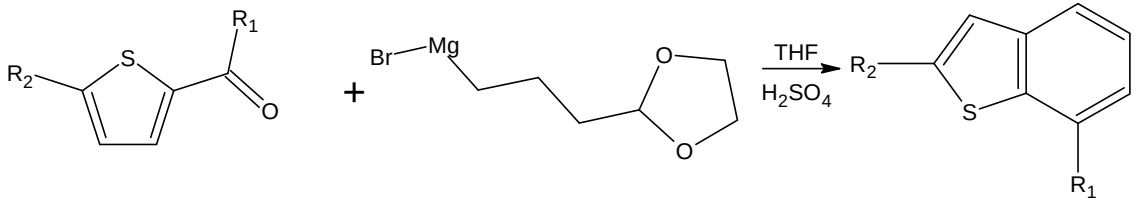




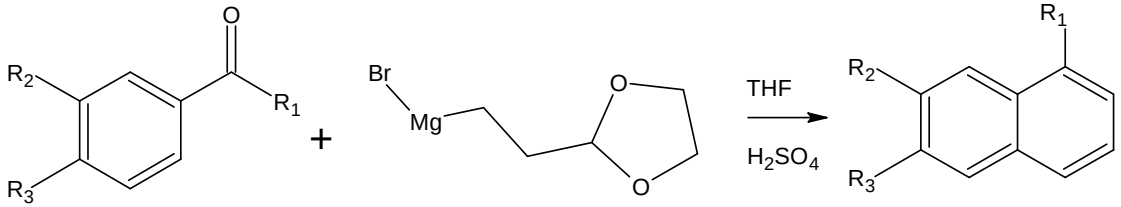
Cyclopentenone
(used in Jasmone industry)



Dopaminergic
D3 Antagonist
WO 951674



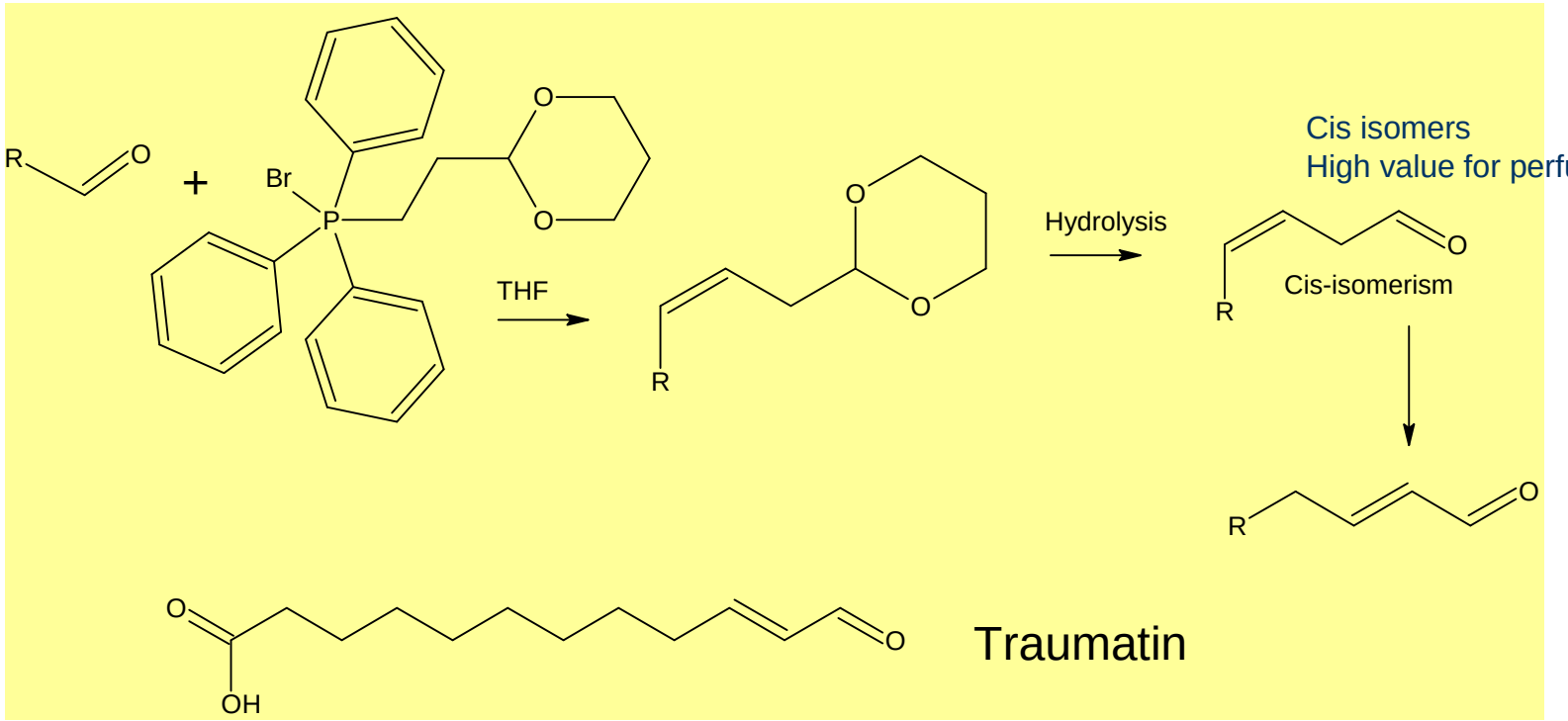
Benzothiophenes

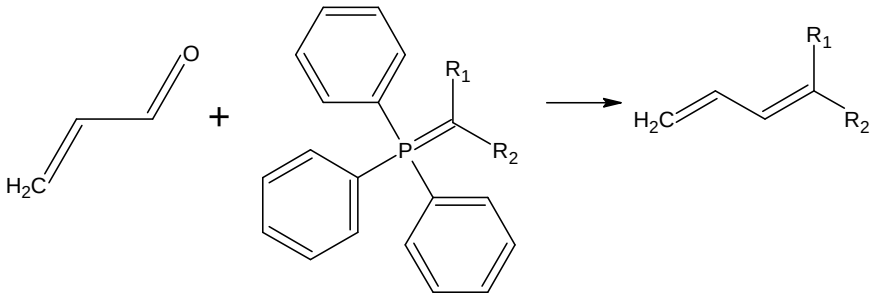


Naphthalenes

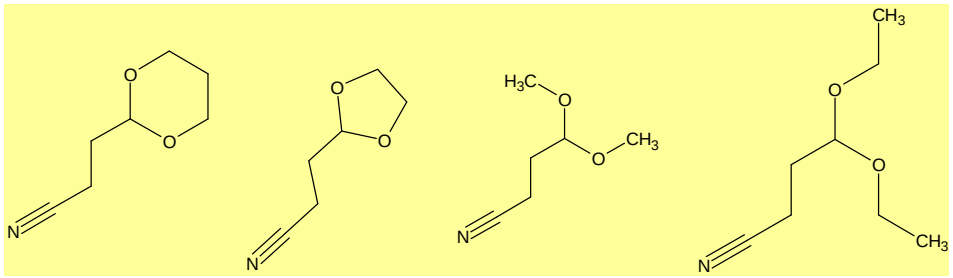
Salts and the Wittig Reaction

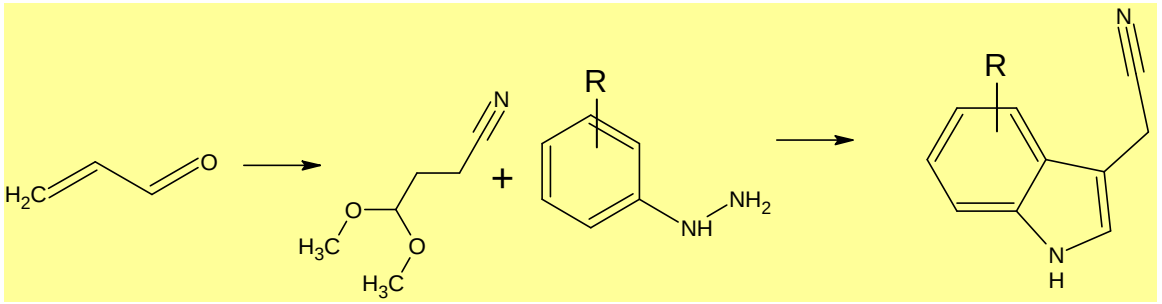
BED and BEDO react easily with triphenylphosphine to form the correponding phosphonium salt

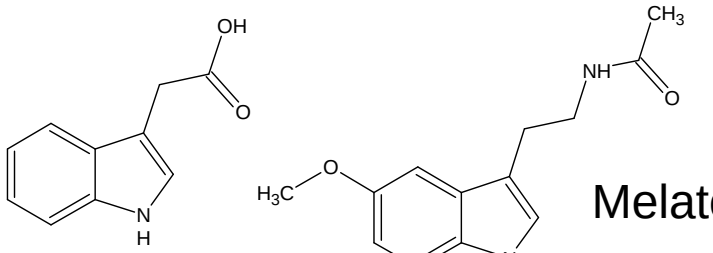




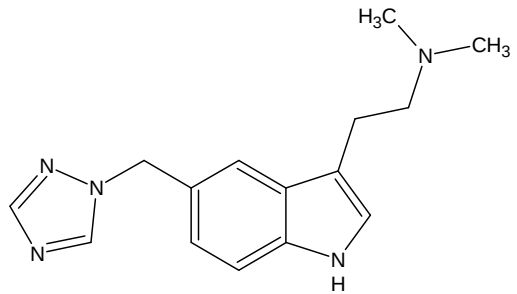
Tryptamines



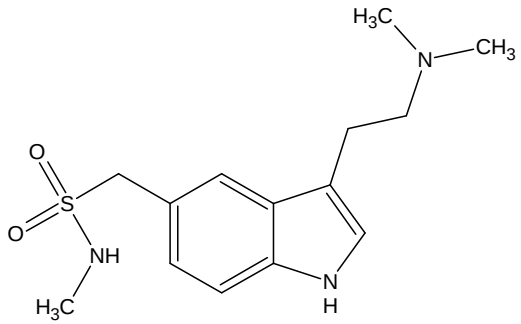




Melatonin

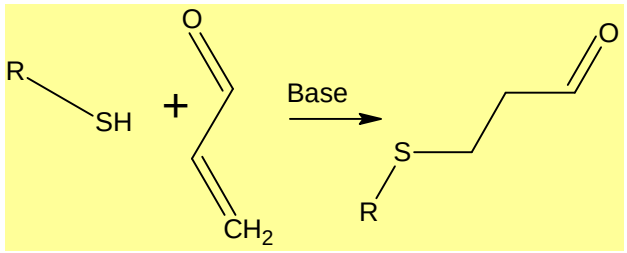


Sumatriptan

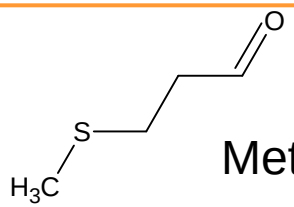


Rizatriptan

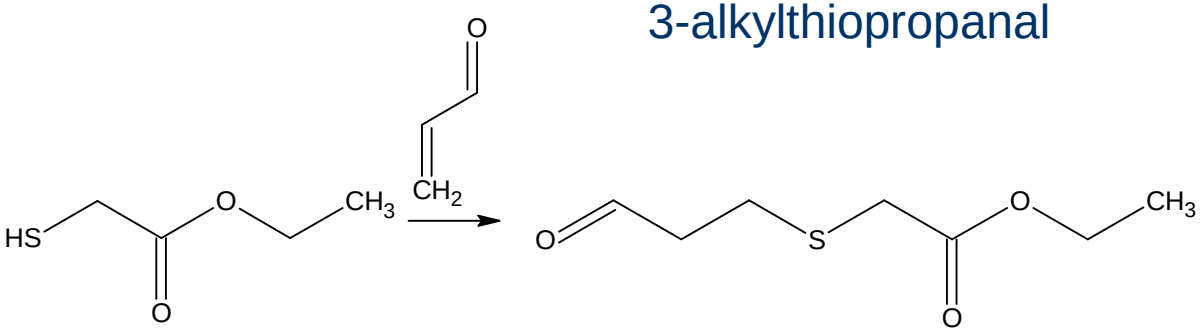
Thiols

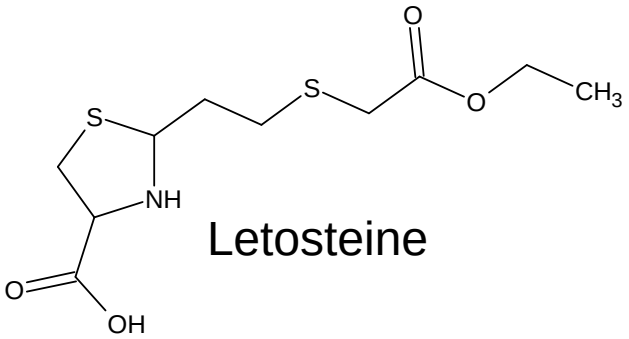


3-alkylthiopropanal

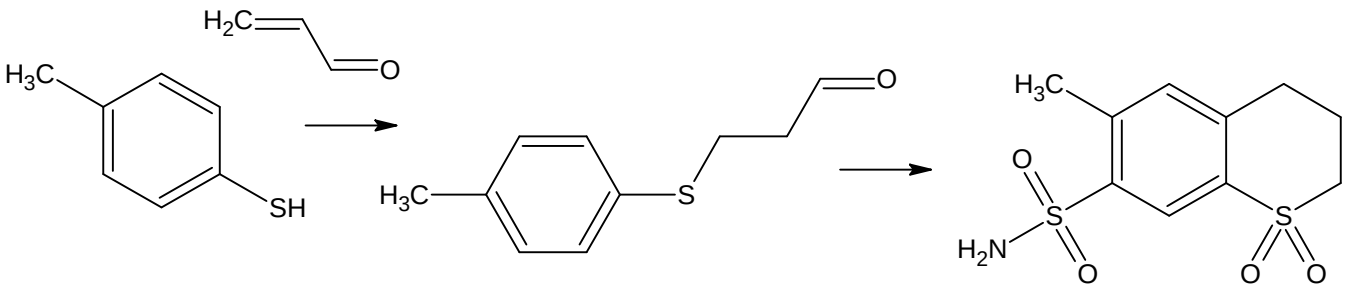


Methional → Methionine



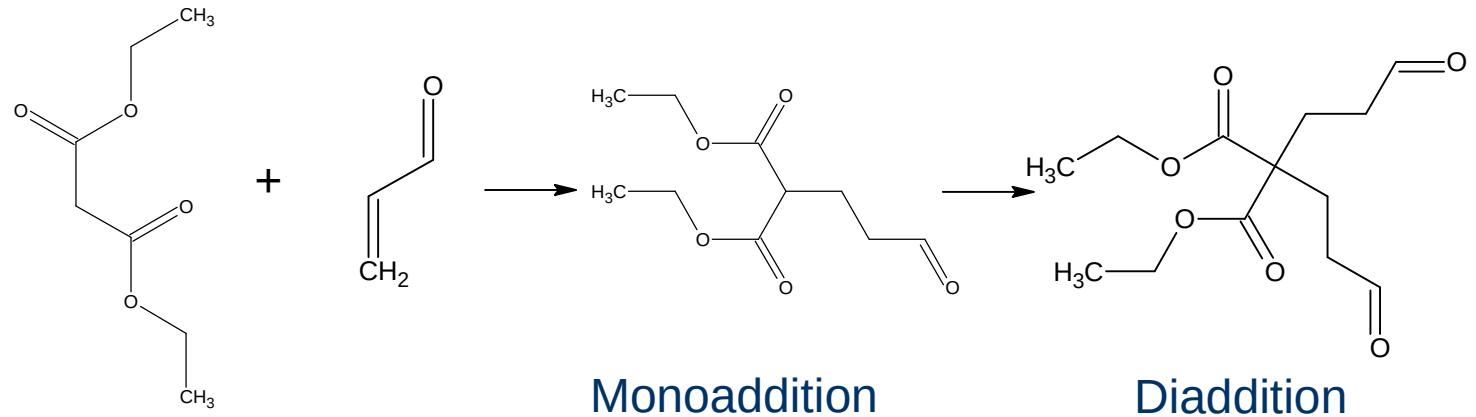


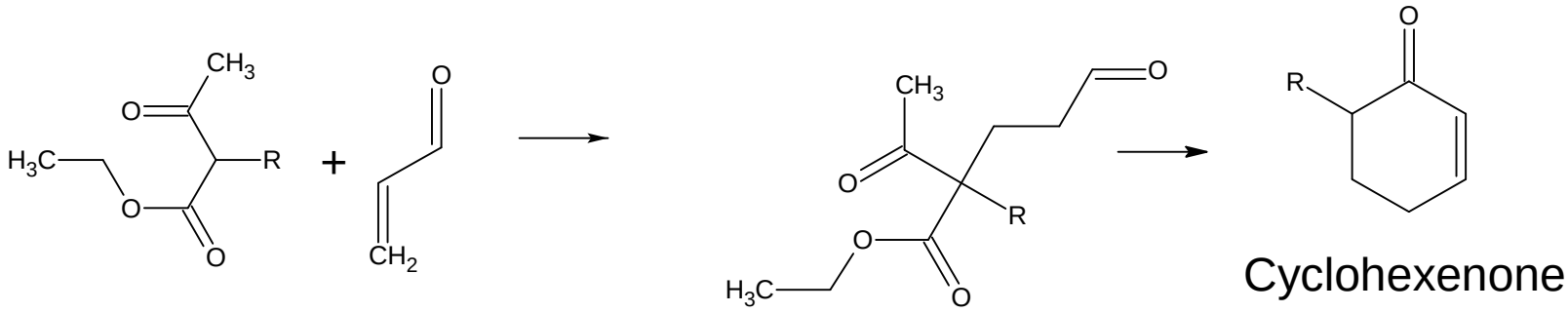
Letosteine

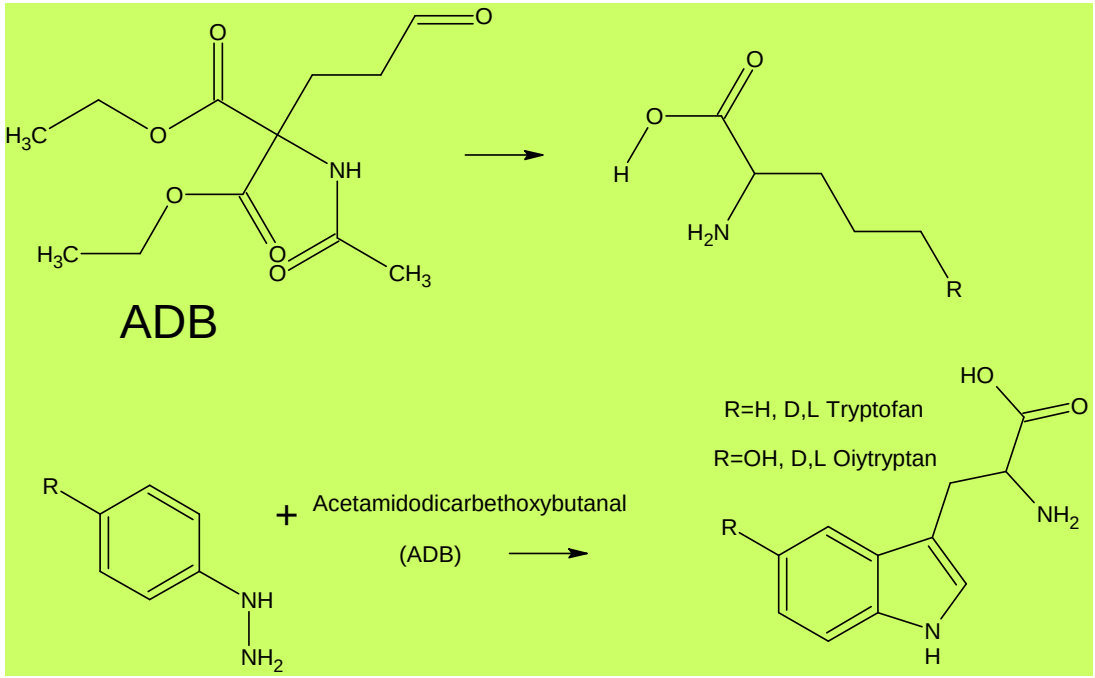


Meticran (diuretic)

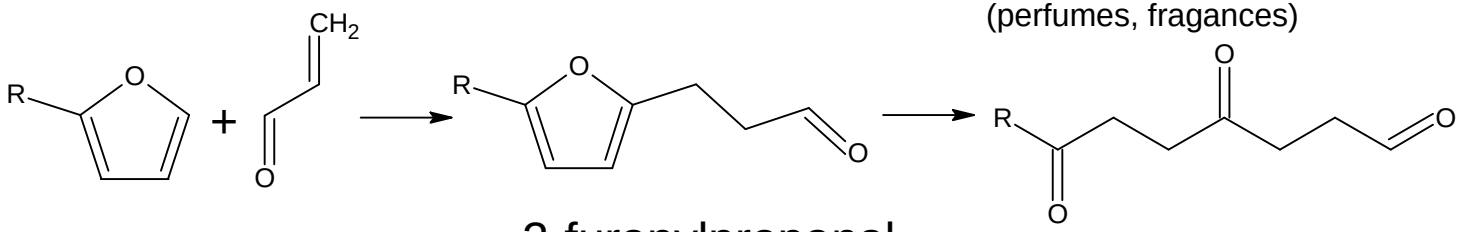
Michael Condensation





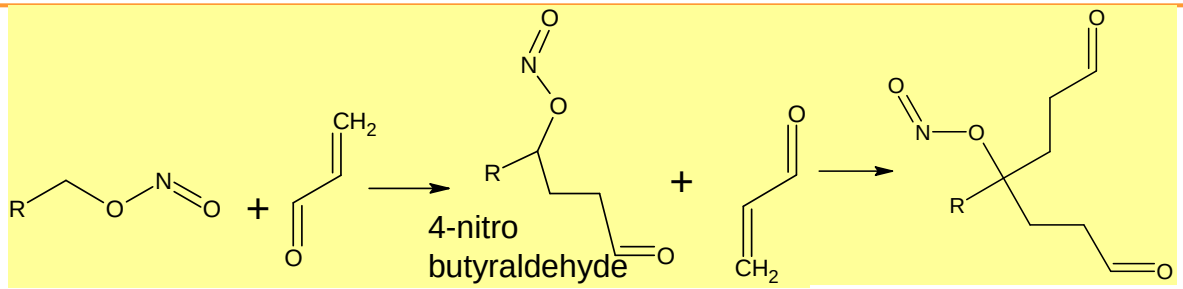


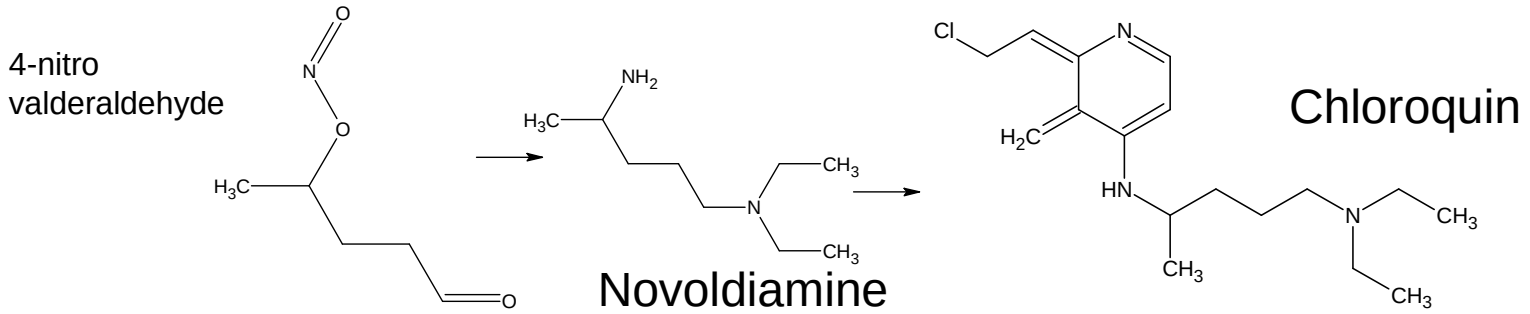
4-oxo heptanedial derivative
(perfumes, fragances)

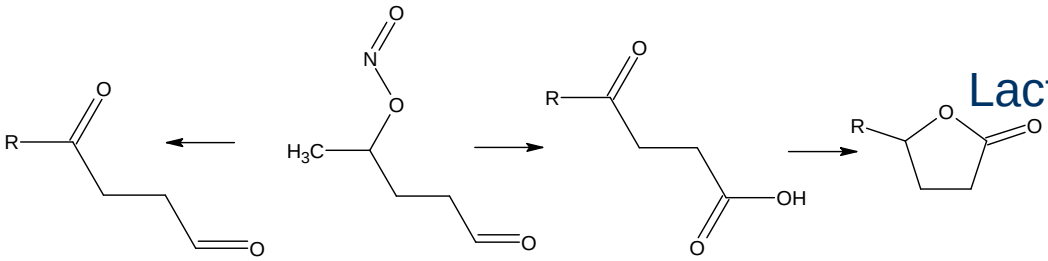


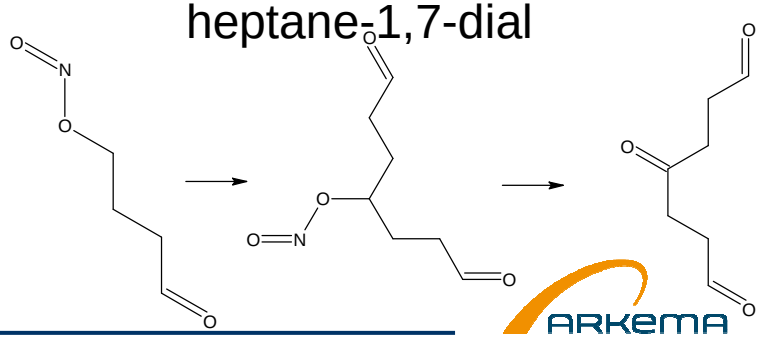
2-furanylpropanal

Nitrated derivatives









For more informations

- Kirk-Othmer Encyclopedia
- Ullmann's Encyclopedia of Industrial Chemistry
- « Fine Chemistry and Acrolein », B. Goyau, Chimica OGGI/*Chemistry today*- November/December 1999
- Info Chimie Magazine, N°412, Oct 1999, p90-98

Arkema's offer

- Bio-based acrolein technology for licencing
  - PILOT scale (Several kg/hr) end 2011
- Partnership on a case by case basis.

- Design parameters:
  - Plant capacity
  - Product quality (acceptable impurities)
  - Location
  - Based on crude or refined glycerine

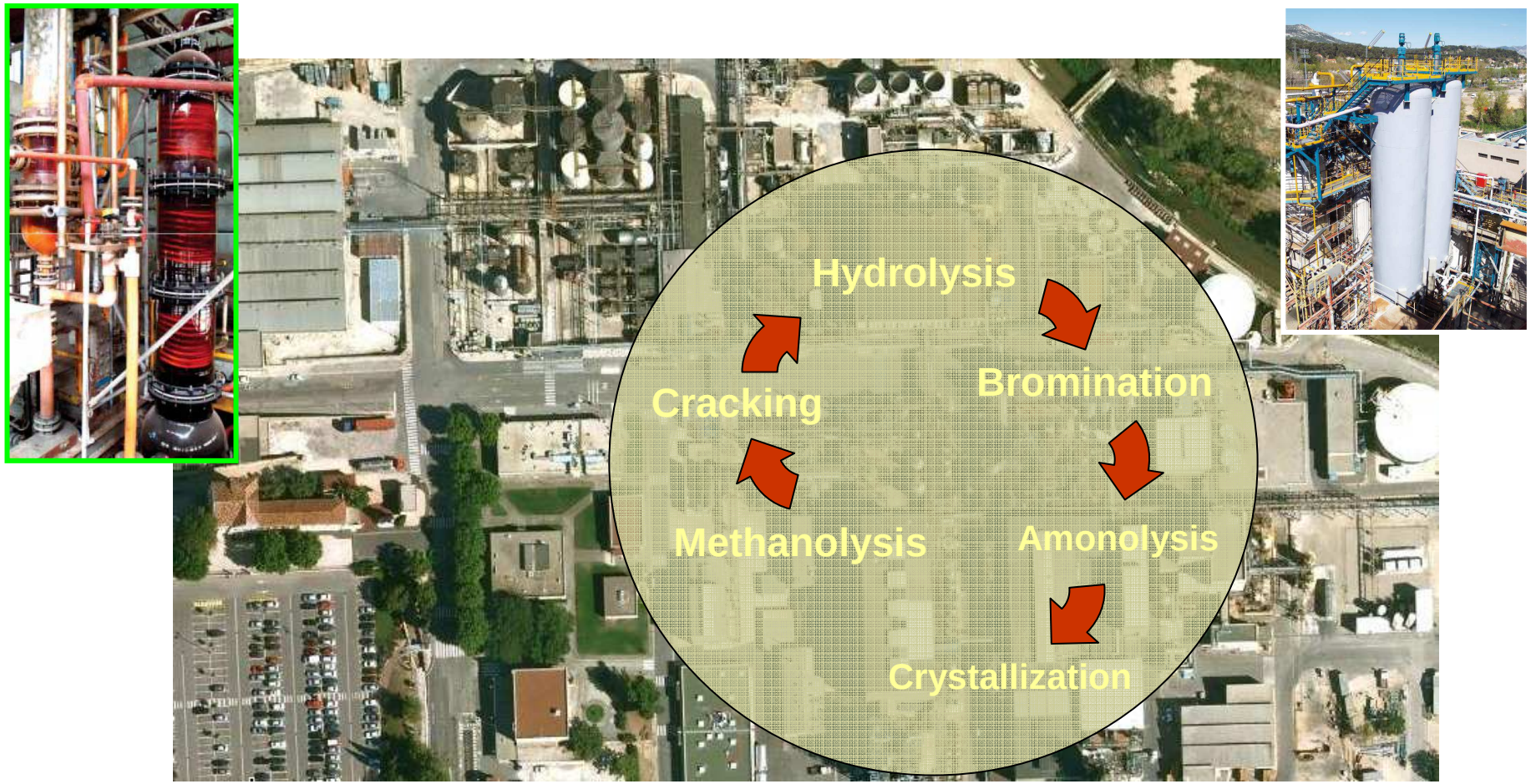
The world is our inspiration

Valorization of Castor Oil for Polymer and Fine Chemicals Applications in Arkema's Castor Biorefinery

Edible vs Non-edible Oils / Fatty acid types

Seeds	C16:0	C18:0	C18:1	C18:2	C18:3	Other	Iodine Nr
Rape seed (v. low erucic)	*3-6*	*1-3*	*55-67*	*16-26*	*6-14*		96-117
Safflower (high linoleic)	*3-6*	*1-4*	*11-21*	*73-79*	*tr*	*0.2*	*140-150*
Safflower (high oleic)	*3-6*	*1-4*	*73-79*	*10-16*	*tr*		*90-110*
Jatropha Curcas	*12-17*	*5-10*	*37-63*	*19-41*		*1-2 C20*	*93-107*
Castor	***1-2***	***1-2***	***3-4***	***5-6***	***0.5-1***	***87-88 (C18:1, OH)***	***82-90***
Pongamia pinnata	*3-8*	*2-9*	*44-71*	*10-18*		*15-20 (C20~C24)*	*80-96*
Rubber seed	*7-11*	*9-12*	*18-30*	*33-39*	*20-26*		*121-148*
Sal	*5-9*	*34-48*	*34-45*	*2-3*		*6-12 C20*	*33-45*
Neem Oil	*13-16*	*14-24*	*49-62*	*2-16*	*-*	*1-3 C20*	*65-80*

Arkema's Castor Biorefinery
Marseille Saint-Menet, France



Flowsheet
Aminoundecanoic acid production

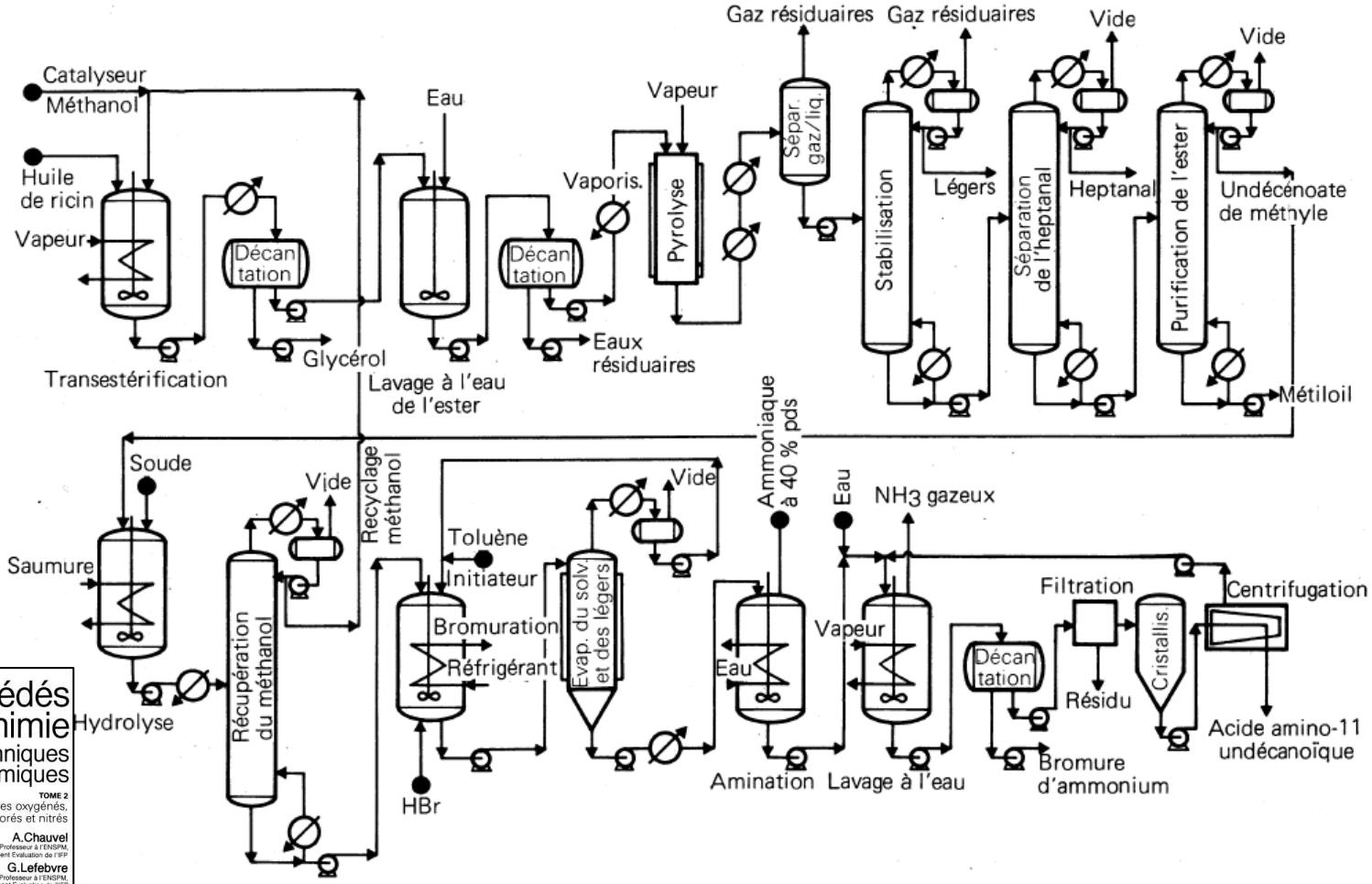
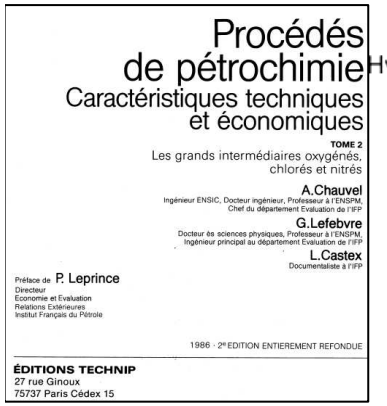


Fig. XII.17. Production de l'acide amino-11 undécanoïque. Procédé Ato.



LES MONOMERES POUR LA SYNTHESE DES POLYAMIDES

ARKEMA
The world is our inspiration

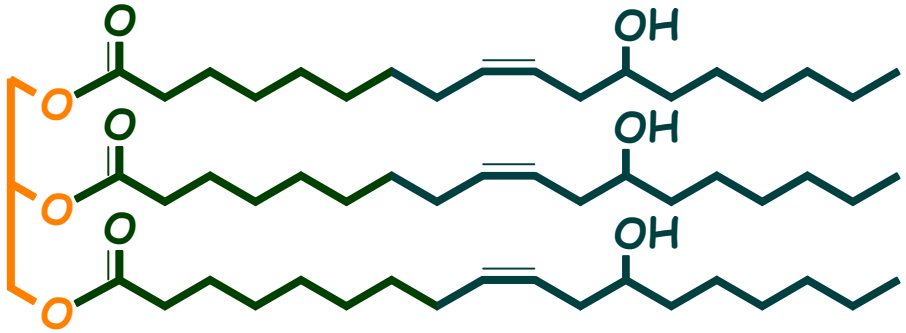
Castor

- Castor is indigenous to the Mediterranean Basin, Easter Africa and India.Today it is widespread throughout tropical regions.In areas with a suitable climate (tropical regions), castor establishes easily and can often be found on unused land.

Castor oil … chemically unique

Castor Oil is the only vegetal oil containing an hydroxyl group in the triglyceride structure.

TRIGLYCERIDE



Castor Beans seeds contains 40 to 60 % of oil wich is made of 80 to 85 % of ricinoleic acid.

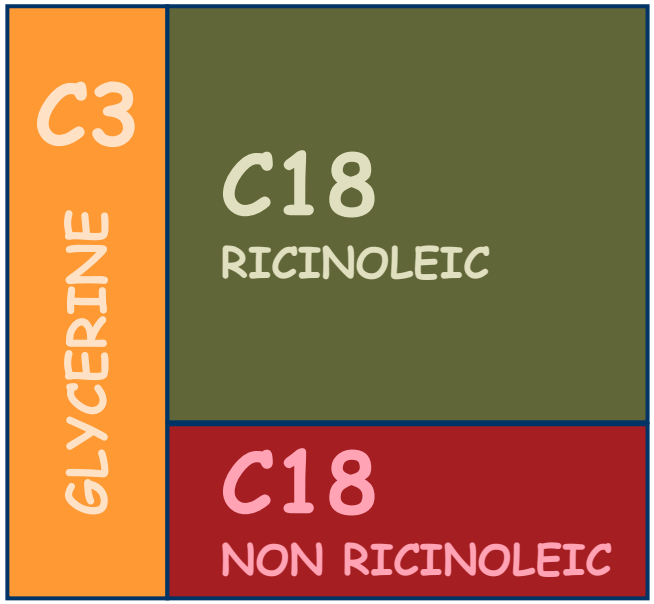
This such particular structure is the key to explain the result of this equation :

18 = 11 + 7 or 10 + 8 …

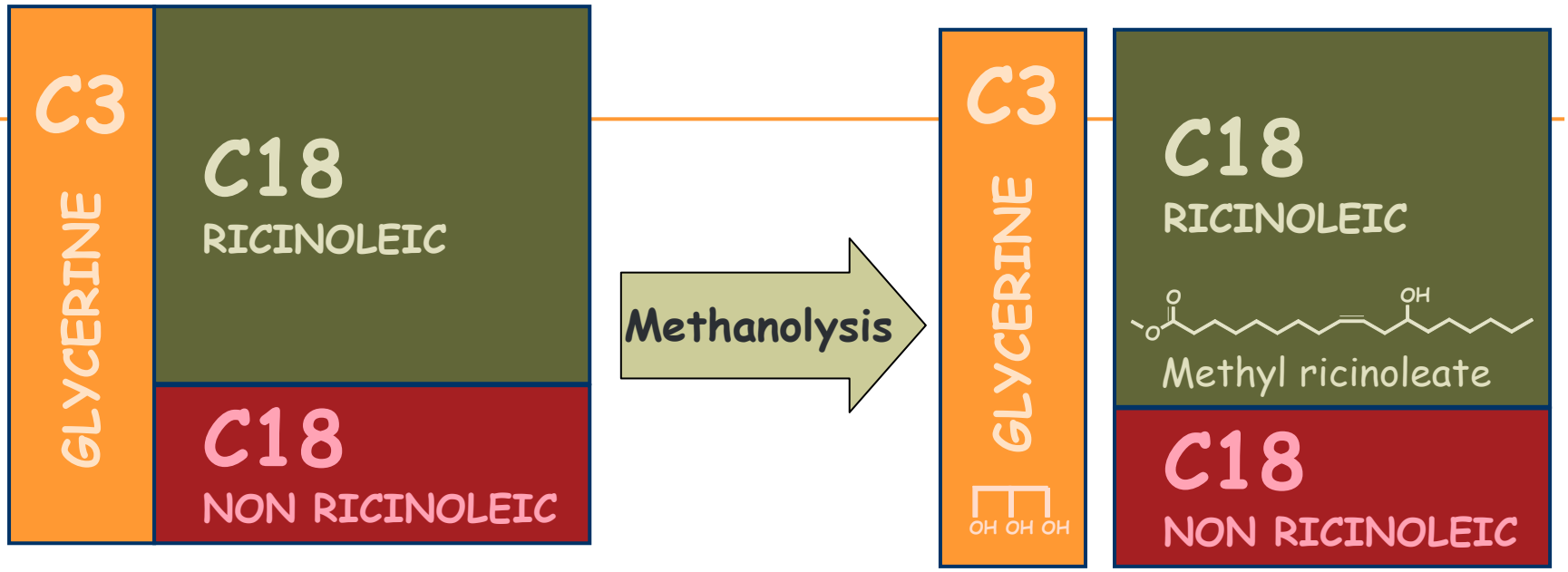
When 18 equals to 11 + 7 …

The behaviour of Castor Oil when heated to high temperature has intrigued chemists since 1845. Since that time Castor Oil chemistry has evolved significantly. The process in use at the Arkema Marseille plant is in fact unique in the world. Castor Oil is a biodegradable and renewable resource for a large range of raw materials.

Castor Oil



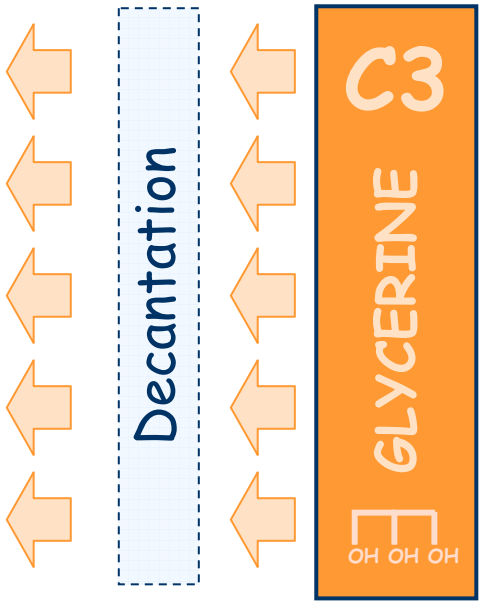
Mixture of Fatty acids triglycerides



Valorisation of glycerine :

- wetting and lubricating agent in handcreams, suntan lotionsand soaps hair care.

- anti-freezing,
- bio-resourced compounds such as acrolein, propylene glycol …

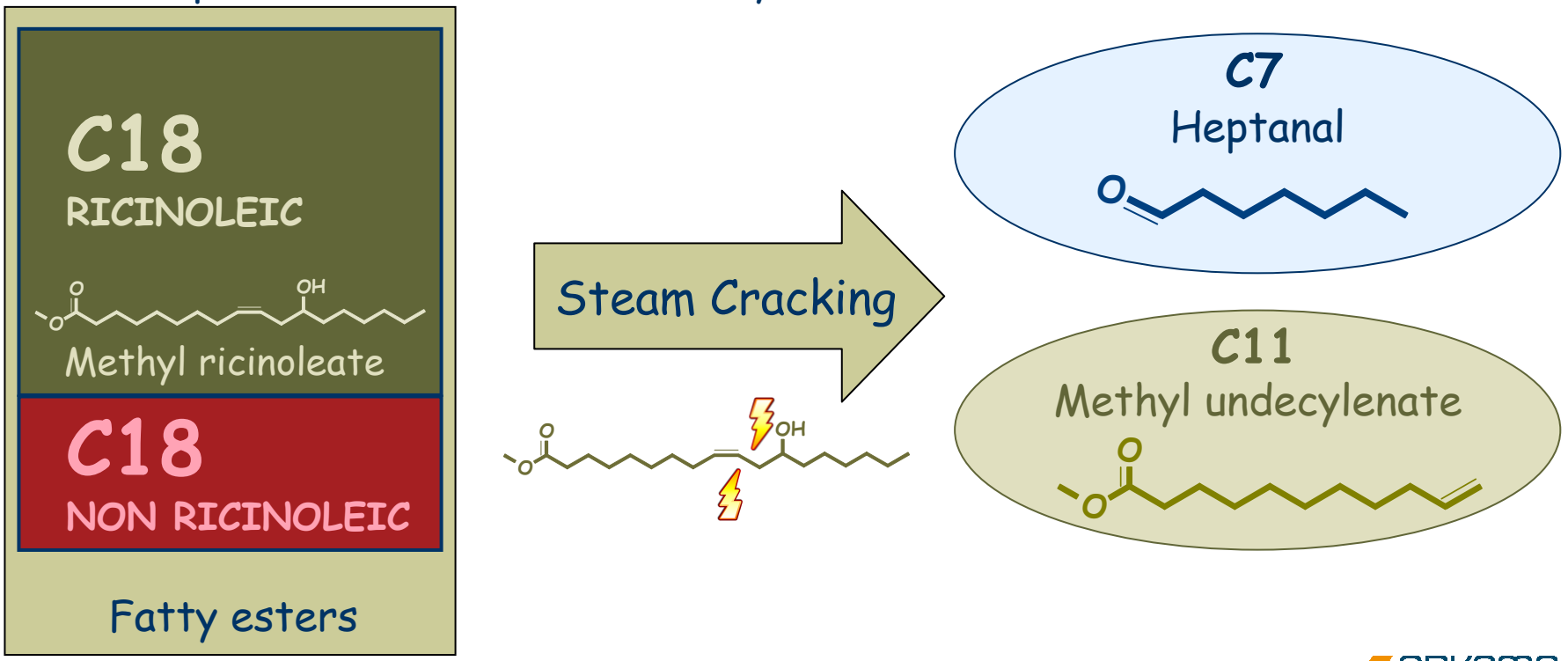


Steam Cracking

When 18 equals to 11 + 7 …

Steam Cracking (pyrolysis at elevated temperature) cleaves ricinoleic acid ester into two parts: one part consisting of 7 carbon atoms and the other of 11 carbon atoms. The Marseille process equation is C18 = C11 + C7.

A whole range of innovative chemistries and end use products are generated from these base reaction products. These products are used in every-day life, to improve our comfort and safety.



C7 derivatives
… from perfumes to technical products

The C7 molecule has seven aligned carbon atoms and is known for the olfactory qualities of certain of its derivatives. In its natural state, it is present in wine as oenanthol.

The low freezing point of this chain makes it well suited for lubricant applications.

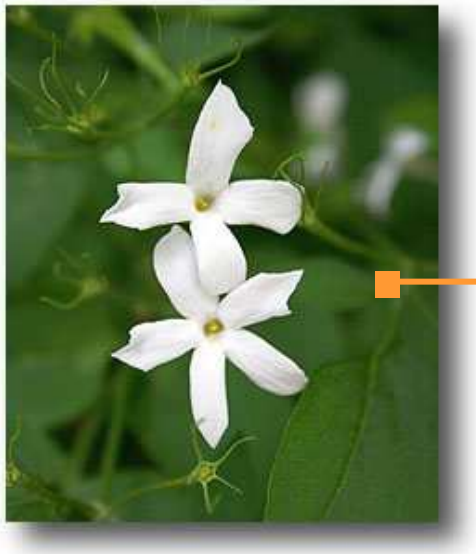
Aldehyde, alcohol and acid are the three main chemical derivatives of C7.

Main characteristics :

- 100% linearity (compared to synthetic route)
- high purity
- 100% bio-based raw material

Applications of heptanal

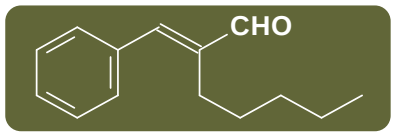
Synthesis intermediate for the fragrance and aroma industry.



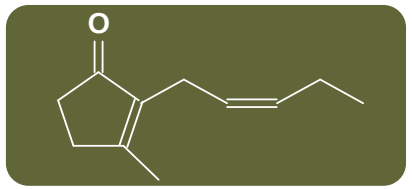
An perfume aromas related to C7 aldehyde is **JASMINE**. This aroma is detectable in many washing powders, soaps, candies and other jasmine perfumed products.

- natural odor : fresh, green, like vegetable
- methyl-heptyne carboxylate : green and floral note

- ACA : α n-amyl cinnamic aldehyde : synthetic jasmine



- Jasmonoids



Applications of heptanol

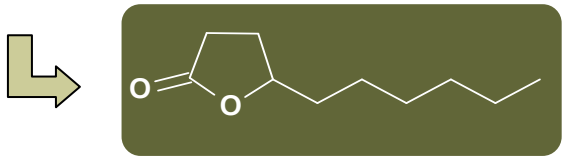
red. → OH

Synthesis intermediate in the fragrance and aroma industry (with fruit taste)

Trace quantities are used in perfumes to provide a peach-apricot aroma.

- γ-decalactone :

  coconut, vanilla flavour (dairy products, beverage)



- Esters with fruit notes (heptyl butyrate, octanoate …)

Synthesis intermediate for plasticizers for polymers.

ARKEMA
The world is our inspiration

Applications of heptanoic acid

The diversity of applications of this acid is surprising :

- Valorised in the form of esters as lubricant for military aircraft jet engines, car engines and refrigerant.

→ compared to C6/C8/C10 analogues

- better compromise in terms of low viscosity at low temperature and low volatility at high temperature,
- very low color
- 100% linear saturated acid,
- lower pour point,
- higher viscosity index.

- High efficiency of C7 salts as corrosion inhibitor (water based hydraulic fluids for automotive, additives in paints, cutting oils, metalworking fluids).

Applications of heptanoic acid

- Chemical intermediates for Pharmaceuticals and cosmetics
  - emollient agent / surfactant in personal care (propylene glycol diheptanoate, stearyl heptanoate …) and in pharmaceutical gel (neopentylglycol diheptanoate)

- Chemical intermediates for aromas and perfumes.

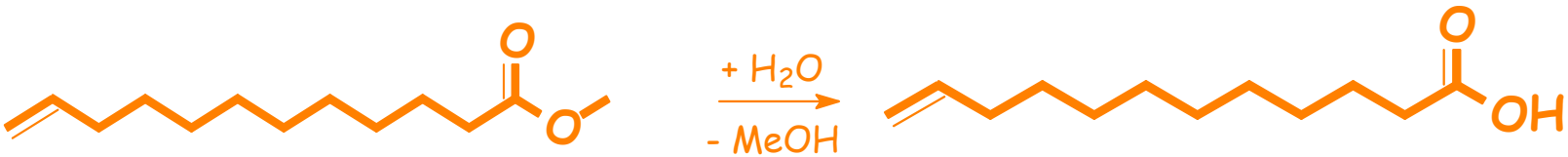
  - natural, green grassy and fruity ester like odour in banana flavours and in coffee, dairy products, passion fruit …

- Synthesis intermediate for plasticizers for polymers.
- Improves the properties of herbicides.

C11 derivatives

Derivatives of methyl undecylenate have the rare property of being both long and bi functional.

They are versatile molecules for chemical synthesis.



methyl undecylenate

undecylenic acid

Both are used for their natural bioactivity and fungi resistance.

C11 derivatives from pharmaceuticals …

Bioactivity and fungi resistance.

- In nature, trace quantities of C11 acid are found in sweat, tears and hair fats. Under salt form (Zn/Ca), it is used in pharmaceuticals for human skincare preparations.

  ie : - treatment of *athletes' foot*
  - effective against denture stomatitis
  - herpes …

  → combining surfactant as well as natural bioresistance properties

- Bacteriostatic action in baby diapers.

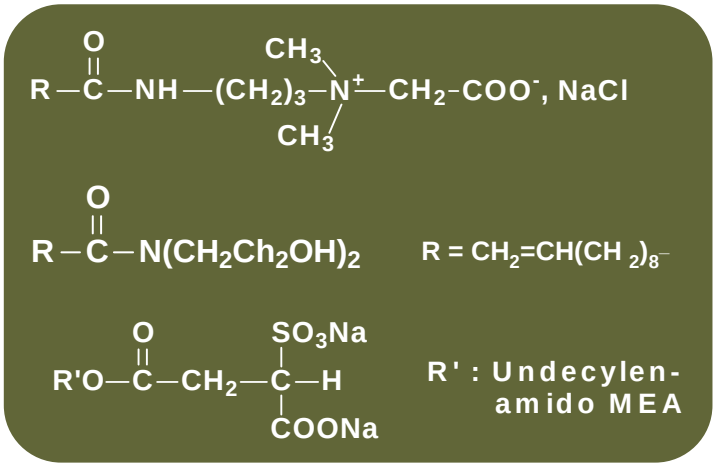
One of the safest, ecological, most economical and highly effective natural bacteriostatic and antifungal agents

C11 derivatives
… Cosmetics – Personal Care …

- Hair care / anti-dandruff shampoos
- Deodorant
- Beauty creams
- (antiseptic) Soaps
- Bacteriostatic emulsifier for cosmetics

→ as surfactants, like

- Betain C11 = Amphoram U (CECA)
  undecylenamido propyl betaine
- undecylenic acid diethanolamid
- disodium undecylenamido MEA-sulfosuccinate



… safe and natural bacteriostatic agent compared to chemical biocides (imidazoles, tolnaftates) used in cosmetics.

C11 derivatives

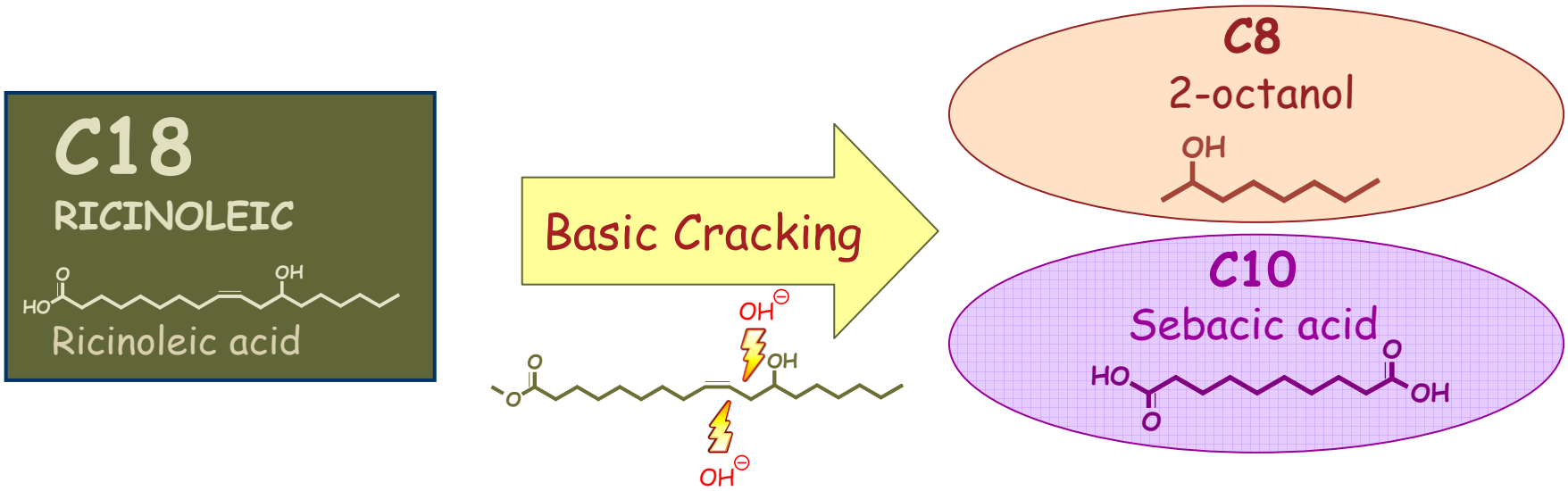
… to Perfumes

- Undecylenic Acid (fruity-rosy note)
- Methyl Undecylenate (heavy citrus note) for lilac based perfumes and anti-odors.
- Chemical intermediates for perfumes.
  - Undecenal for rose or jasmine based formulations, key component for quality perfumes (fixing agent) and quality enhancer for large volume products.
  - Undecenol (citrus, floral note), volume / natural freshness to floral compositions, effect increasing, especially in soap formulations.
  - Macrocyclic musks

    ie : Cyclopentadecanolid
    (Exaltolide, Pentalide, Thibetolide)

When 18 equals to 10 + 8 …

In a second step, ricinoleic acid is cleaved to give capryl alcohol (2-octanol) and sebacic acid (C10 α,ω-diacid).



Properties and uses of 2-Octanol

The 2-octanol (capryl alcohol) is mainly used as a raw material for producing intermediates in flavors and perfumes industry.

In cosmetics, it is an intermediate for the preparation of caprylic/capric triglyceride (CCT) use as emollient, excellent as a super-fatting oil in soap-making and improves spreading of skincare formulas.

Capryl alcohol can be used as a possible alternate for 2-ethylhexanol or isooctyl alcohol in the preparation of diesters plasticizers : dicapryl esters such as dioctyl phthalate (DOP), dioctyl adipate (DOA).

2-octanol is used as a solvent. It is also used as a mineral floatation agent and for producing emulsifiers, defoaming and anti-bubbling agents.

Challenges in Chemistry from vegetable oils « Green Notes for Green Chemistry »

- Development of « Green » chemistry from vegetable oils requires to set the conditions to make money
- Use all parts of vegetable oils:
  - Glycerol
  - Fatty acids
  - ➔ high concentration in targeted fatty acid
  - ➔ dedicated vegetable oils
- Develop Safer processes
- Renewable chemicals with improved Life Cycle Analysis
  - Renewable (bio-based) # biodegradable # safe


Thank you for your attention

No waste, everything is valorised !!!

C18
NON RICINOLEIC

Esterol A is made up of saturated and unsaturated natural fatty acid methylic esters like stearic, oleic or linoleic acid.

Esterol A is mainly used as machining oils due to good lubricating properties (oiliness, anti-wear properties). It finds a lot of applications in a large range of domains :

- Metal working fluids / Cutting oils (lubricity for anti-wear additive when sulfurized),
- Fat liquors for leather treatment,
- Concrete mold release agents (biodegradable, fluid oil, easy to emulsify),
- Grease and lubrication formulations,
- Anti-foaming agents.