聲明

本檔案之內容僅供下載人自學或推廣化學教育之非營利目的使用。並請於使用時註明出處。[如本頁取材自○○○教授演講內容]。

永續化學合成(4)

可再生性資源在合成上的利用

劉廣定

臺大化學系

(ktliu@ntu.edu.tw)

The use of chemicals and solvents from renewable resources

永續化學十二原則 (Anastas and Warner, 1998)

7. A raw material or feedstock should be renewable rather than depleting, whenever technically and economically practicable.

永續工程十二原則(Anastas and Zimmerman, 2003)

7. Material and energy inputs should be renewable rather than depleting.

永續十律 Ten commandments of sustainability (Manahan, 2005)

7. Material demand must be drastically reduced; materials must come from renewable resources, be recyclable and, if discarded to the environment, be degradable.

二氧化碳

無毒(但能令人窒息)

不自燃也不助燃

有高純度之廉價商品

易成液態或超臨界態

易除去或回收再用

可用為溶劑及反應試劑

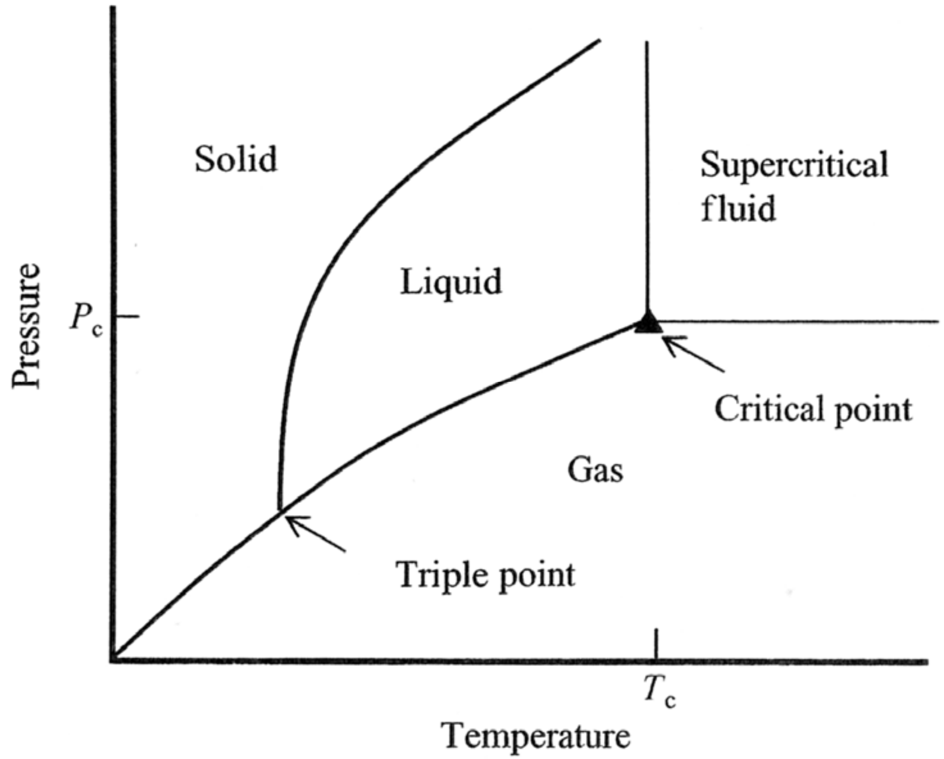
Green Chemistry Using Liquid and Supercritical Carbon Dioxide (DeSimone and Tumas, Ed., Oxford, **2003**)

Green Reaction Media in Organic Synthesis **(**Mikami, Ed., Chapter 4, Blackhill, **2005)**

The Potential of CO_2 in Synthetic Organic Chemistry **(**Rayner, *Org. Proc. Res. Dev.* **2007**, *11*, 121-132)

Alternative Solvents for Green Chemistry (Kerton, Chapter 4, RSC, 2009)

Phase diagram and critical points



Material	T_c (°C)	P_c (bar)
Ammonia	132.4	113.2
Carbon dioxide	31.1	73.8
Ethane	32.2	48.7
Ethene	9.2	50.4
Fluoroform	25.9	48.2
Propane	96.7	42.5
Water	374.2	220.5

Advantages and disadvantages of using CO_2 as a solvent

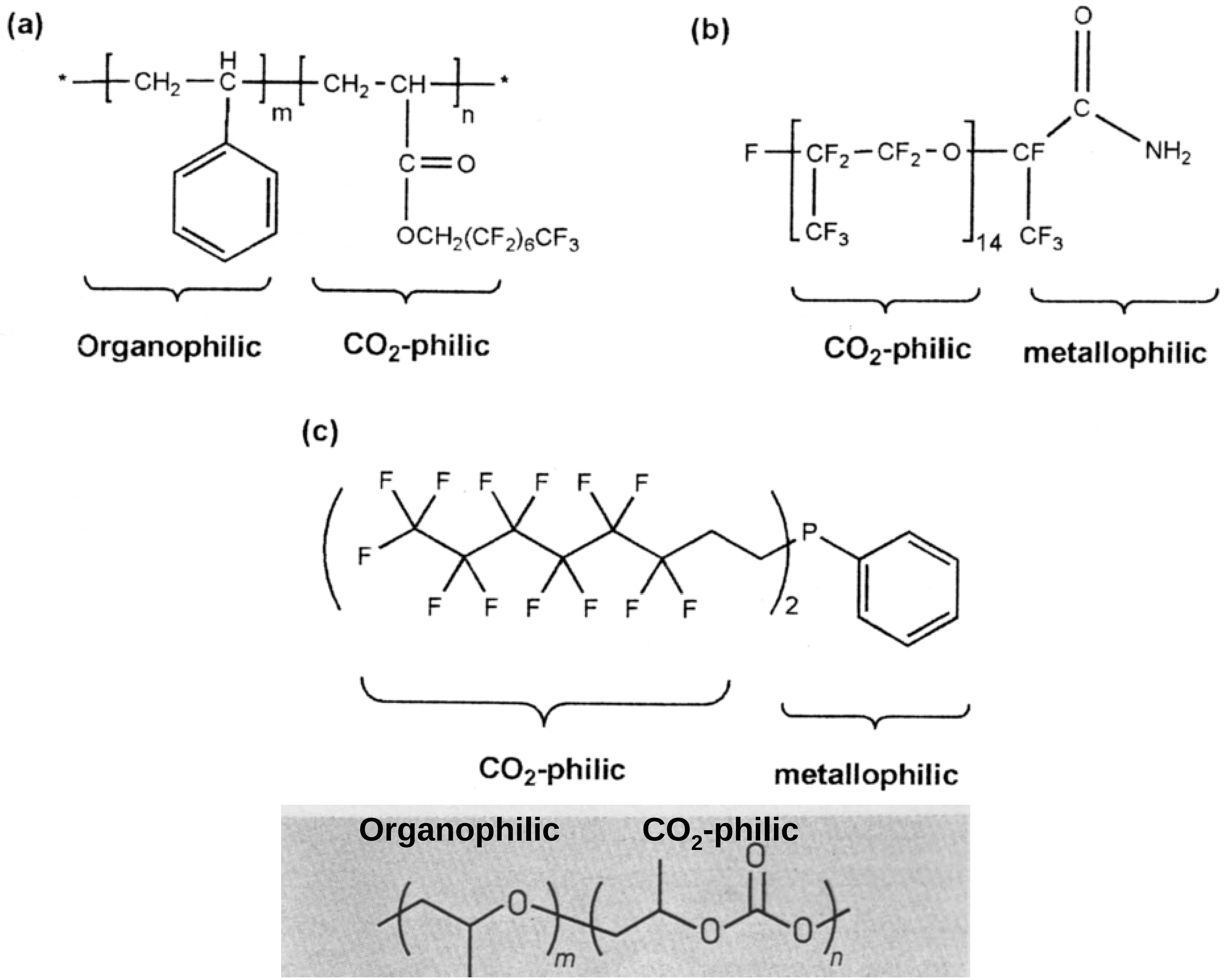
Advantages	*Disadvantages*
Non-toxic	Relatively high pressure equipment
Easily removed	Equipment can be capital intensive
Potentially recyclable	Relatively poor solvent
Non-flammable	Reactive with powerful nucleophiles
High gas solubility	Possible heat-transfer problems
Weak solvation	
High diffusion rates	
Ease of control over properties	
Good mass transfer	
Readily available	

(Lancaster, *Green Chemistry* Table 5.3)

Liquid CO_2 (50-60 bar, rt): Application in dry-cleaning, etc.; relatively little studied, many potential benefits

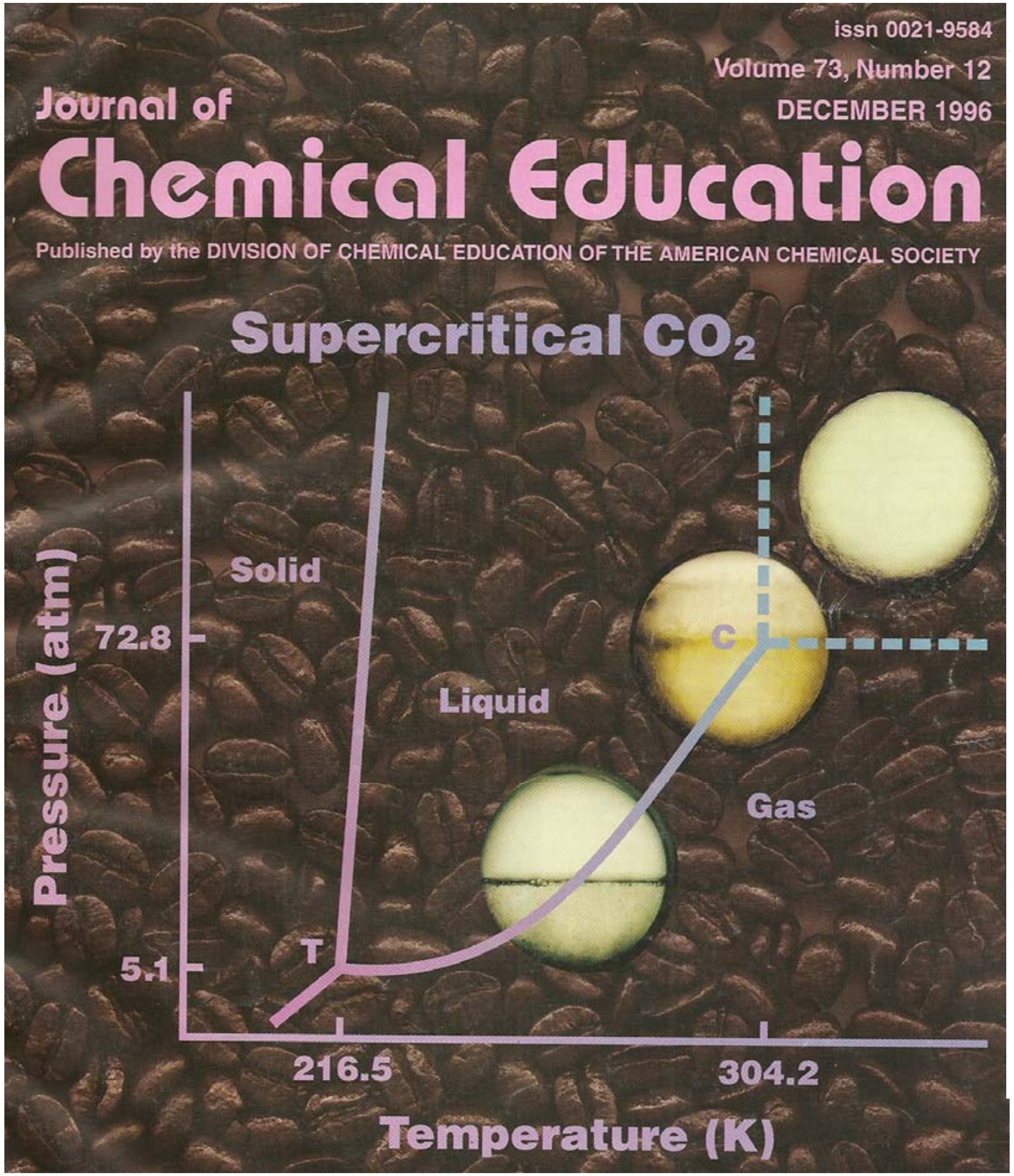
Supercritical fluid CO_2 (＞74 bar, ＞31℃): Application in decaffeination; natural product extraction, any many more

Solvents for SCF-CO_2



Non-fluorinated (ether-carbonate) copolymer by Beckman and coworkers at U. of Pittsburgh. **PGCC Award of 2002**

“老” 技術



化工技術

1998年10月號／第67期

超臨界流體技術　專輯　　　　談駿嵩主編

Research: Science & Education

Chemical Reactions in Supercritical Carbon Dioxide

C. M. Wai, Fred Hunt, Min Ji, and Xiaoyuan Chen
Department of Chemistry, University of Idaho, Moscow, ID 83844-2343

J. Chem. Educ. **1996**, *75*, 1641-1645

Research: Science and Education

Making Nanomaterials in Supercritical Fluids: A Review

Xiangrong Ye and C. M. Wai*
Department of Chemistry, University of Idaho, Moscow, ID 83844-2343; *cwai@uidaho.edu

J. Chem. Educ. **2003**, *80*, 198-204

Supercritical Fluids for the Fabrication of Semiconductor Devices: Emerging or Missed Opportunities?

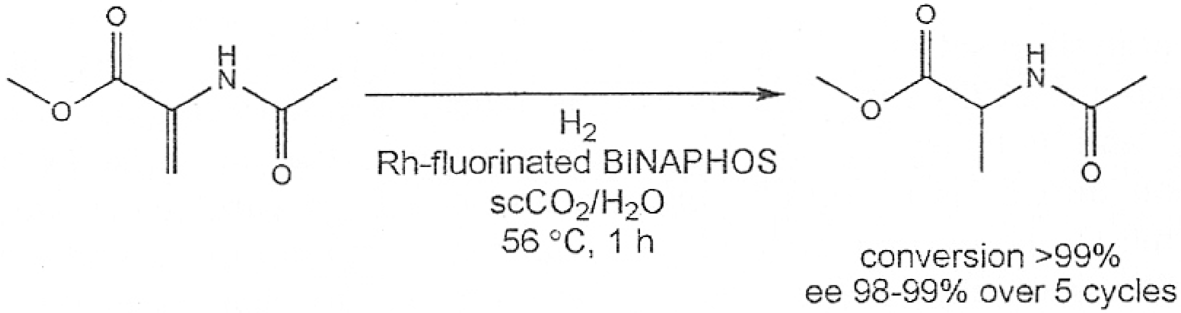
Alvin H. Romang and James J. Watkins*

Polymer Science and Engineering Department, University of Massachusetts—Amherst, Amherst, Massachusetts 01003

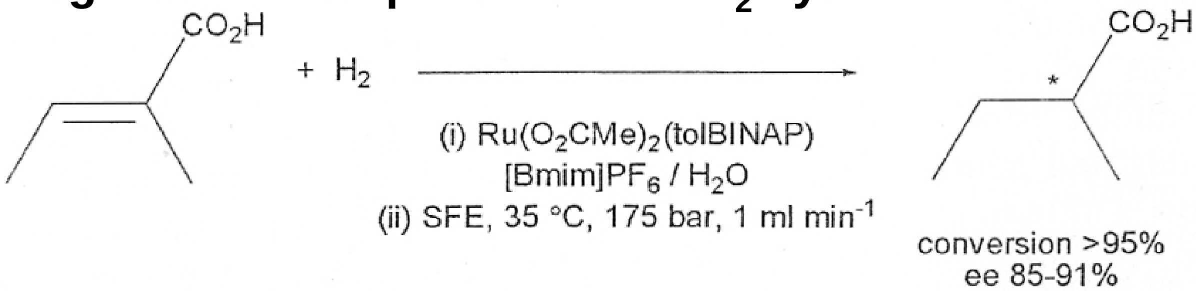
Chem. Rev. **2010**, *110*, 459-478

Examples

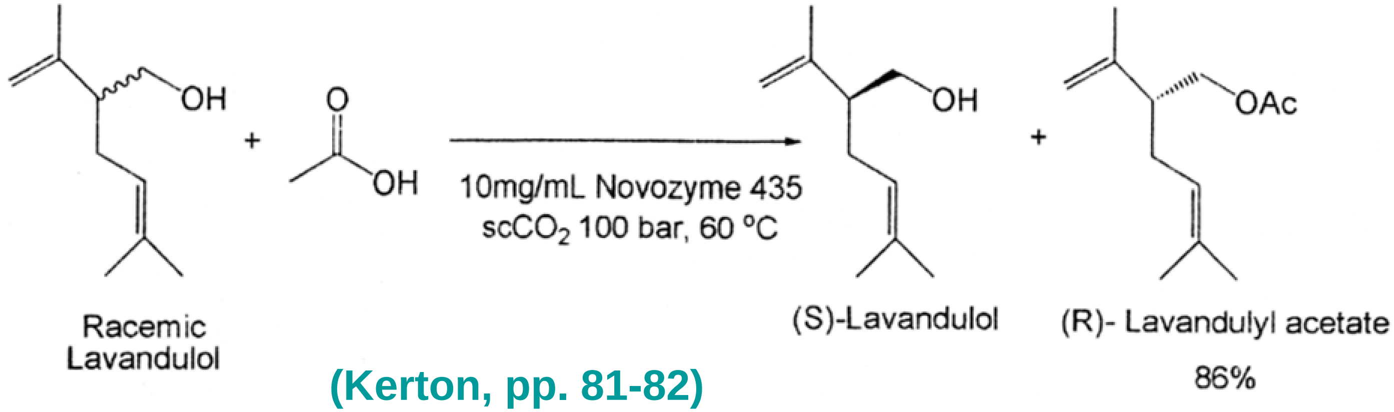
Enantioselective hydrogenation in $scCO_2$-H_2O system



Hydrogenation in Biphasic IL-$scCO_2$ system



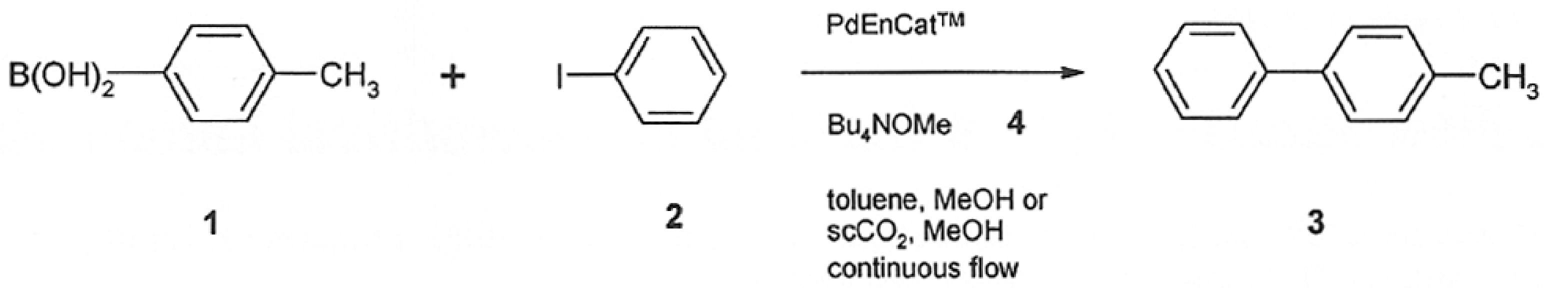
Biocatalytic esterification



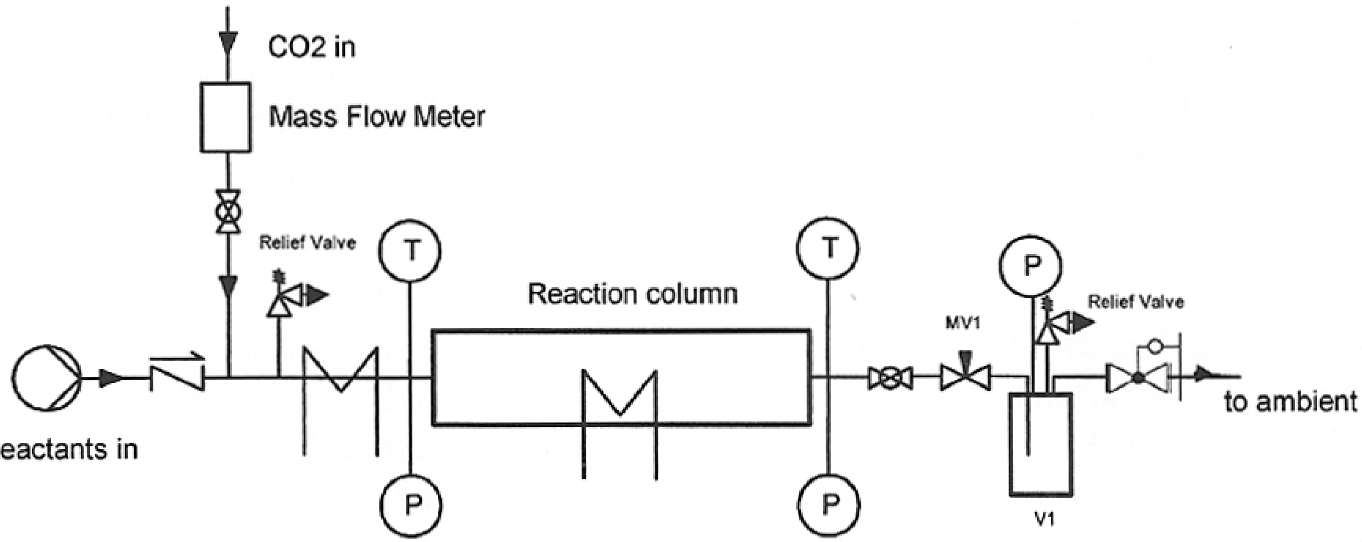
(Kerton, pp. 81-82)

Courtesy of Professor C. M. Wai, U. Idaho.

Continuous-Flow Suzuki-Miyaura Reaction in SCF-CO_2



Suzuki−Miyaura preparation of 4-phenyltoluene 3 under continuous-flow conditions.



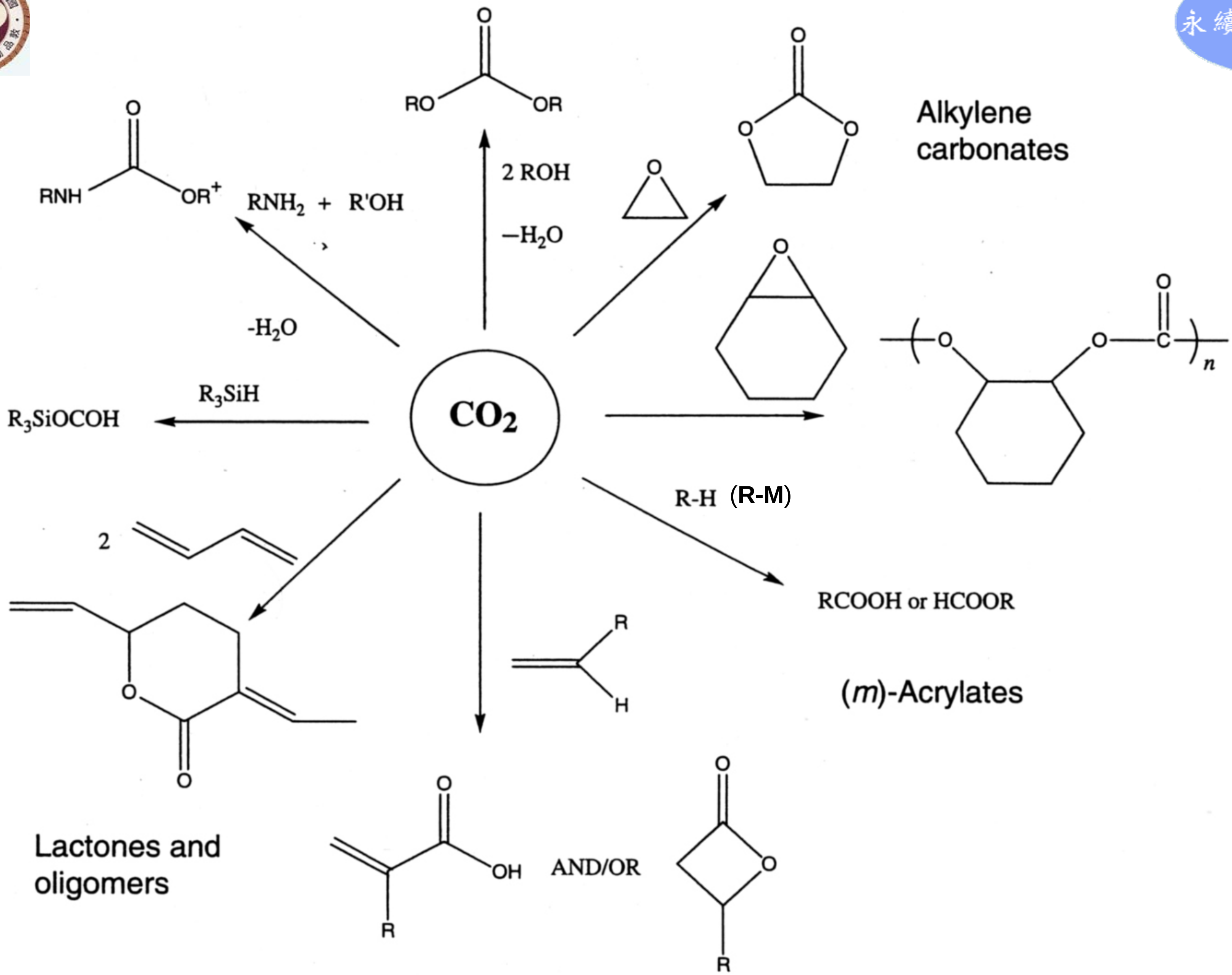
Schematic of continuous-flow apparatus for Suzuki−Miyaura reaction in $scCO_2$.

Lecky, *et al. Org. Process Res. Dev*. **2007**, *11*, 144-148

CO_2 Transformations

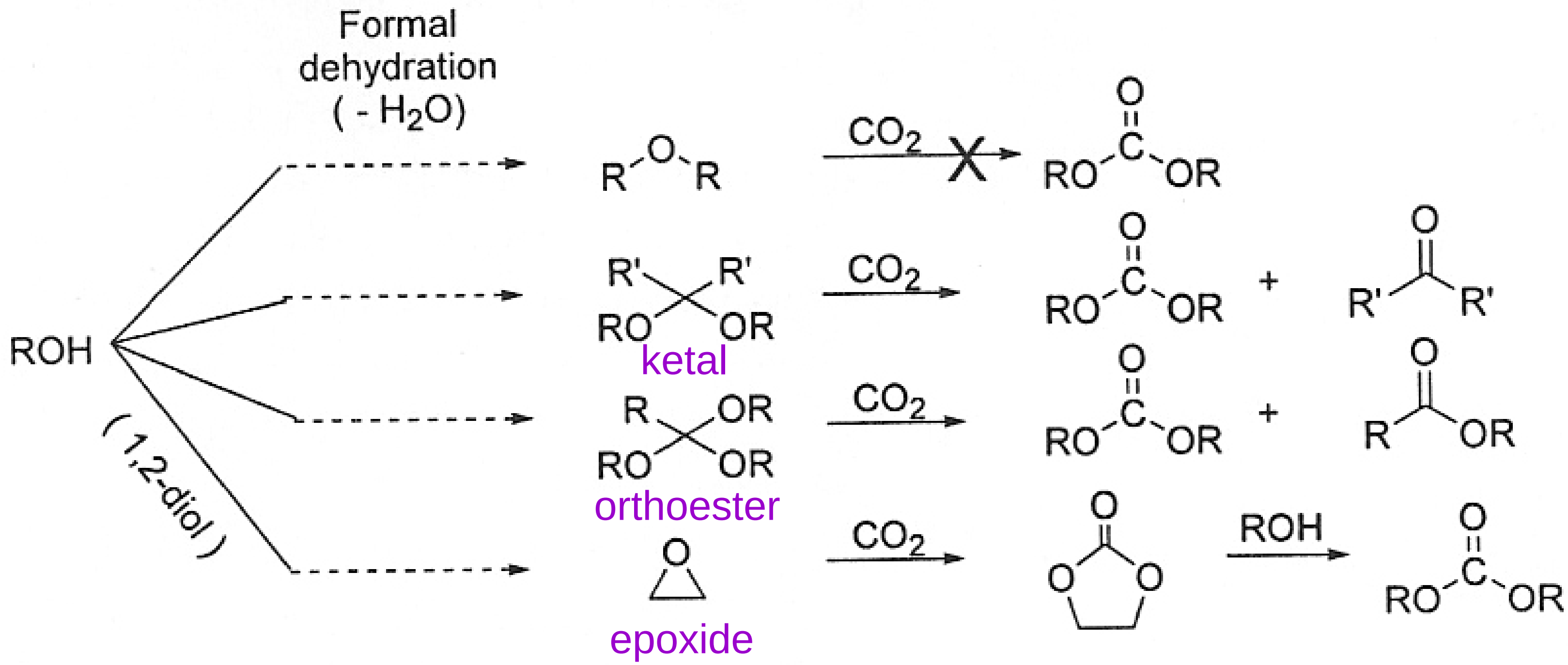
- **Biological** → carbohydrate; HCOOH + CH_3OH
- **Photochemical** → CO, CH_3OH, HCOOH, etc.
- **Electrochemical** → CO, CH_3OH, HCOOH, etc.
- **Reforming** → **CO + H_2**
- **Inorganic** → **M_2CO_3**
- **Organic** → a variety of products
  via reduction or carboxylation, etc.

(Sakakura, Choi and Yasuda, *Chem. Rev.* **2007**, *107*, 2365-2387)



CO2
2 ROH
−H2O
RO
OR
Alkylene carbonates
RNH
OR+
RNH2 + R'OH
-H2O
R3SiH
R3SiOCOH
R-H (R-M)
RCOOH or HCOOR
(m)-Acrylates
2
Lactones and oligomers
OH
AND/OR
R
H

Dialkyl carbonate from CO_2



Production of dimethyl carbonate from ethylene oxide and CO_2 as a more effective way for the reuse of CO_2

(*Clean Technologies and Environmental Policy* **2009**, *11*(*4*), 459-472)

Dimethyl Carbonate as a Green Reagent

Low toxicity, no mutagenic or irritating effect.

Biodegradable (＞90% in 28 days)

Melting point (°C)	4.6
Boiling point (°C)	90.3
Density (d_4^{20})	1.07
Viscosity (μ^{20}, cps)	0.625
Flashing point (°C, O.C.)	21.7
Dielectric constant (ε^{25})	3.087
Dipol moment (μ, D)	0.91
ΔH vap (kcal/kg)	88.2
Solubility H_2O (g/100g)	13.9
Azeotropical mixtures	With water, alcohols, hydrocarbons

Useful methylation and alkoxycarbonylation agents

≦90 C $\quad PhOH + CH_3OCOOCH_3 \xrightarrow{\text{Cat. base}} PhOCH_3 + CO_2 + CH_3OH$

≧160 C $\quad ROH + CH_3OCOOCH_3 \xrightarrow{\text{Cat. base}} ROCOOCH_3 + CH_3OH$

(Tundo and Selva, in *Methods and Reagents for Green Chemistry*, pp. 77-102)

Green chemistry metrics: a comparative evaluation of dimethyl carbonate, methyl iodide, dimethyl sulfate and methanol as methylating agents

(M. Selva and A. Perosa, *Green Chem.* **2008**, *10*, 457-464)

The methylating effciency of DMC, DMS, MeI and MeOH was assessed based on atom economy and mass index. These parameters were calculated for three model reactions: the O-methylation of phenol, the mono-C-methylation of phenylacetonitrile, and the mono-N-methylation of aniline. The analysis was carried out over a total of 33 different procedures selected from the literature. Methanol and, in particular, **DMC yielded very favorable mass indexes** (in the range 3-6) indicating a significant decrease of the overall flow of material (reagents, catalysts, solvents, *etc.*), thereby providing safer greener catalytic reactions with no waste.

$$\textbf{MI} = \frac{\sum \text{reagents} + \text{catalysts} + \text{solvents} + etc.\ (\text{kg})}{\text{Desired product (kg)}}$$

Organic reactions in aqueous media

Reference books and **review articles**:

- Adams, et al., *Chemistry in Alternative Reaction Media*, **2004** , Wiley
- Lindström Ed., *Organic Reactions in Water*, **2007** , Blackwell
- Li and Chan, *Comprehensive Organic Reactions in Aqueous Media,* 2nd Ed, **2007**, Wiley
- Herrerias, *et al.*, *Chem. Rev*. **2007**, *107*, 2546-62 (Reaction of C-H)
- Dallinger and Kappe, *Chem. Rev*. **2007**, *107*, 2563-91 (MW assisted)
- Hailes, *Org. Proc. Res. Dev*. **2007**, *11*, 114-120 (general discussions)
- Kerton, *Alternative Solvents for Green Chemistry,* Chapter 3, **2009** , RSC
- Minakata and Komatsu, *Chem. Rev*. **2009**, *109*, 711-724 (on silica)
- Chanda and Fokin, *Chem. Rev*. **2009**, *109*, 725-748 (on water)

Table 5.4 *Advantages and disadvantages of using water as a solvent*

Advantages	*Disadvantages*
Non-toxic	Distillation is energy intensive
Opportunity for replacing VOCs	Contaminated waste streams may be difficult to treat
Naturally occurring	High specific heat capacity – difficult to heat or cool rapidly
Inexpensive	
Non-flammable	
High specific heat capacity – exothermic reactions can be more safely controlled	
Odorless and colorless (contamination is easy to recognize)	Some compounds or catalysts react with water in an adverse way. Water-soluble catalyst is difficult to recover.

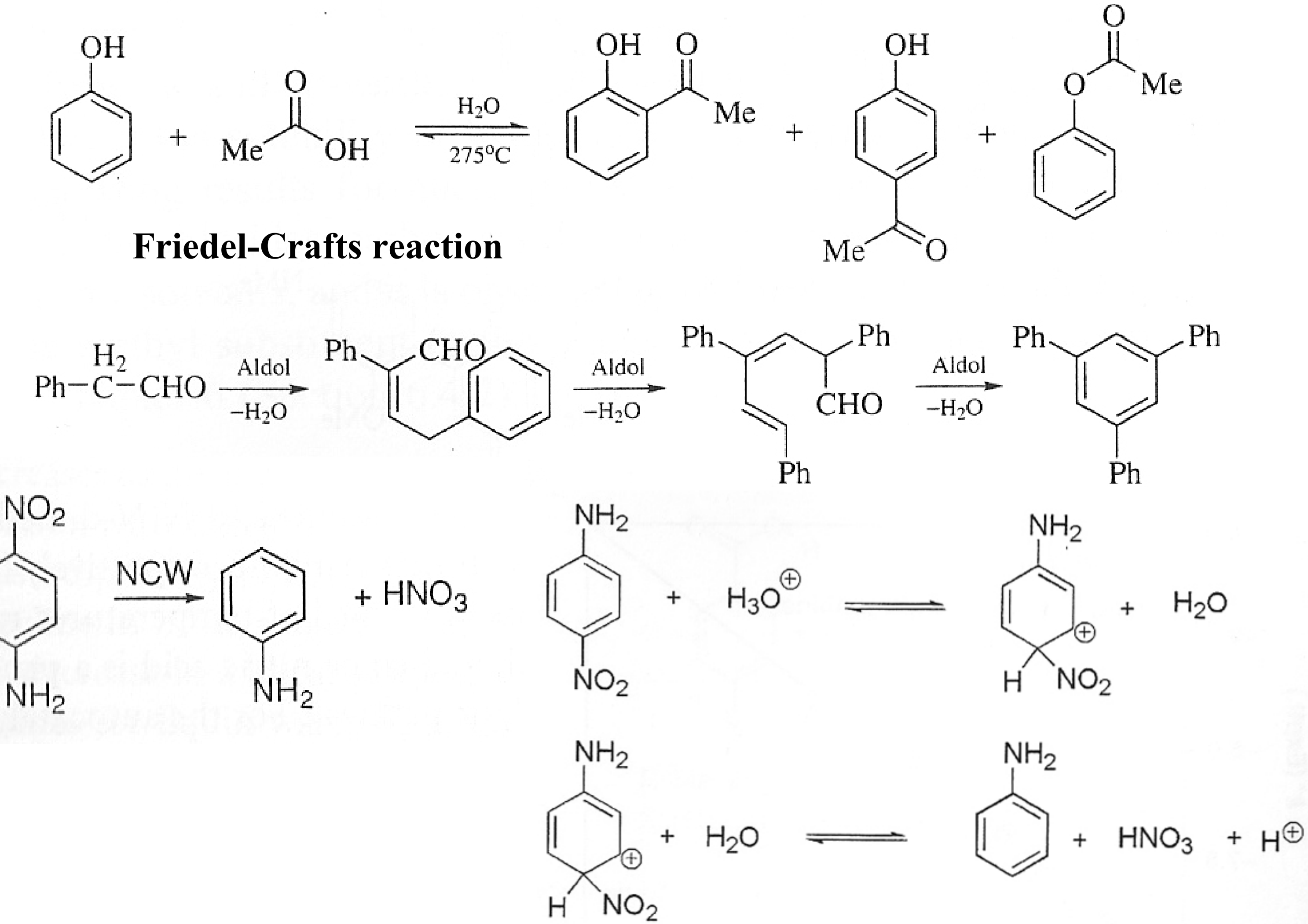
Lancaster, p. 149

Water's dissociation peaks under near-critical conditions

	Ambient	Near-critical	Supercritical
Temperature, °C	25	275 (200-300)	400 (374)
Pressure, bar	1	60	230 (221)
Density, g per cc	1	0.7	0.1
Dielectric constant	80	20	2 (6)
Relative ionization constant[a]	1	1,000	<0.01

[a] $K_w/K_w(25℃)$

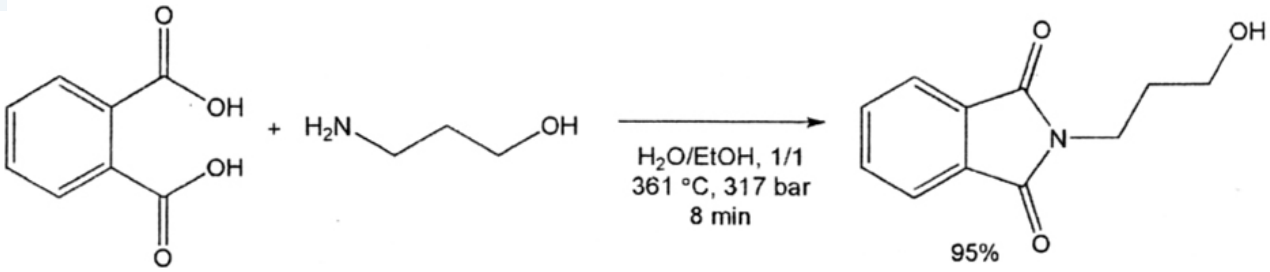
Reactions in near-critical water (NCW)



No acid or base catalyst is required.

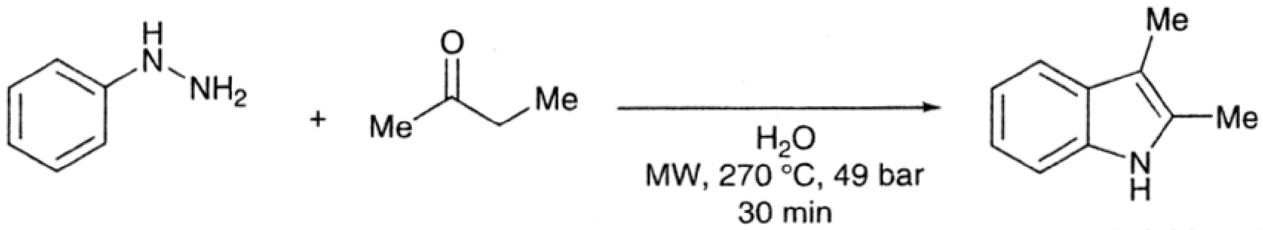
Also for other hydrolysis, hydration, elimination, rearrangement, etc

Phthalimide synthesis at high temperature and pressure



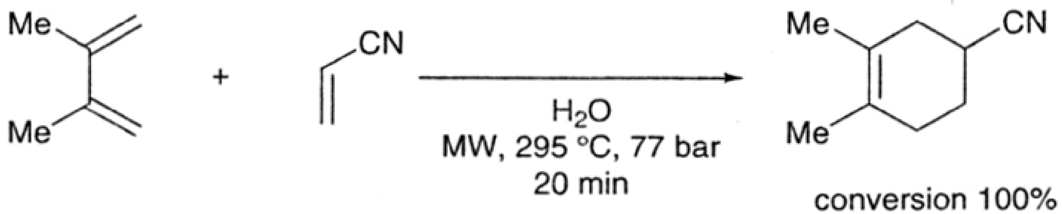
Some microwave assisted reactions at NCW

Fischer indole synthesis



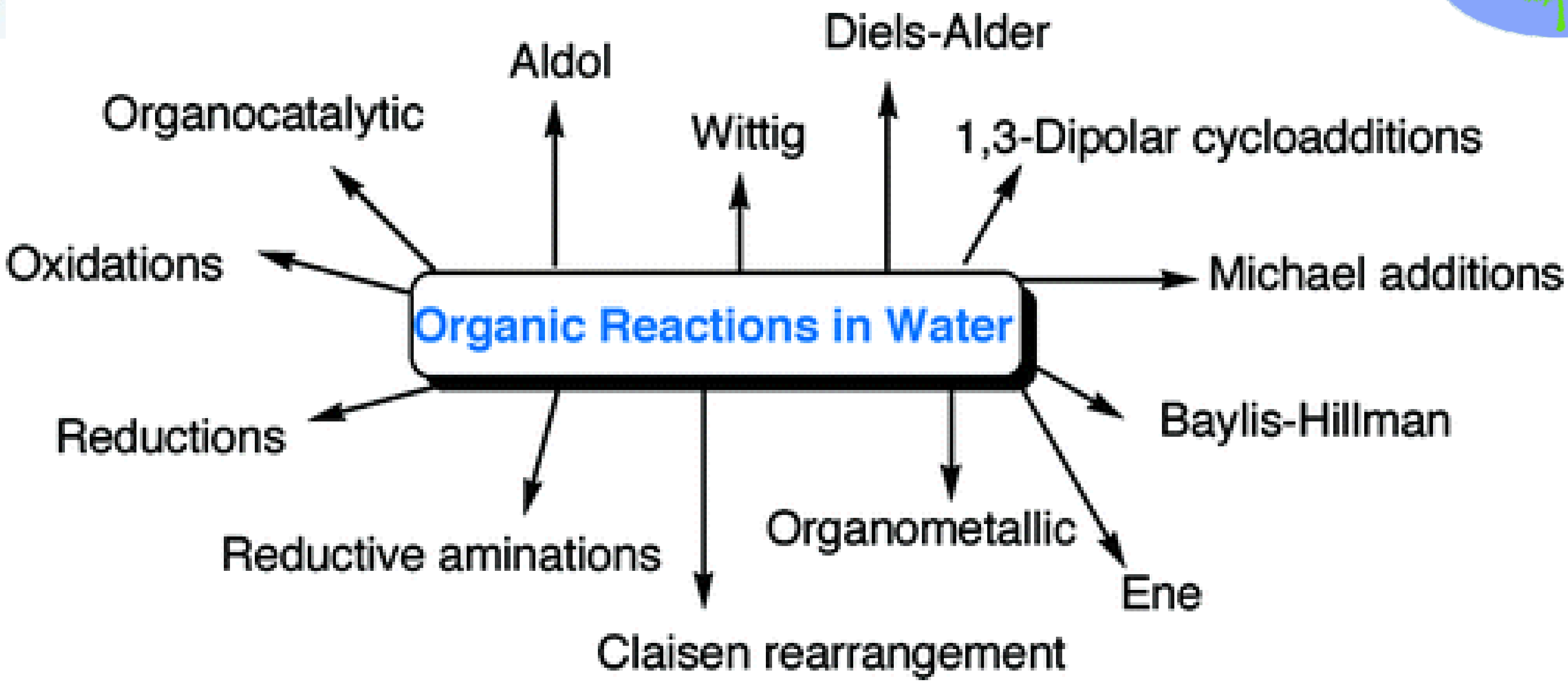
isolated yield 64%
(column chromatography, CH_2Cl_2)

Diels-Alder reaction



conversion 100%
isolated yield 65%
(extraction, Et_2O
chromatography, CH_2Cl_2)

(Kerton, p. 88)



Hailes, *Org. Process Res. Dev*. **2007,** *11*, 114-120

This short review focuses on the potential use of water as a reaction solvent, highlighting advantages and the range of reactions that can be carried out in water.

Hydrophobic Effects

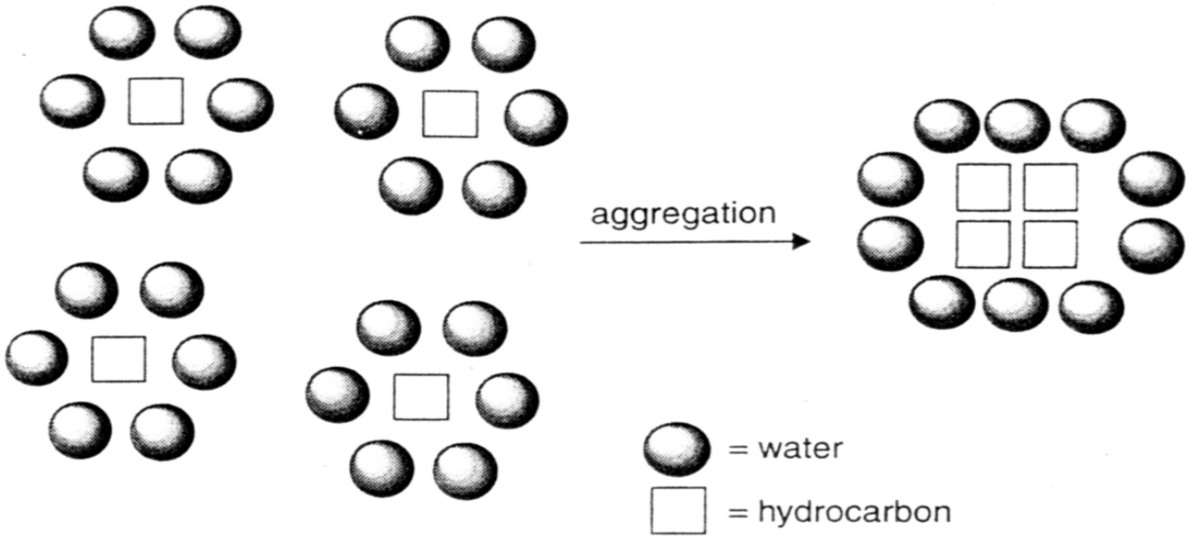
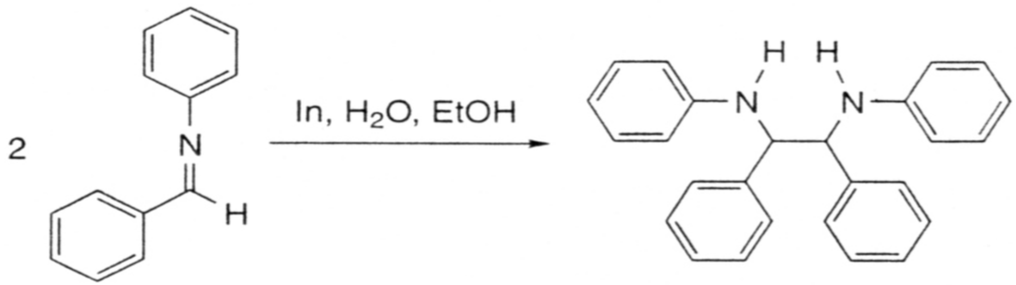


Figure 5.5 The hydrophobic effect. Aggregation of hydrocarbon molecules in water reduces the number of molecules with restricted motion

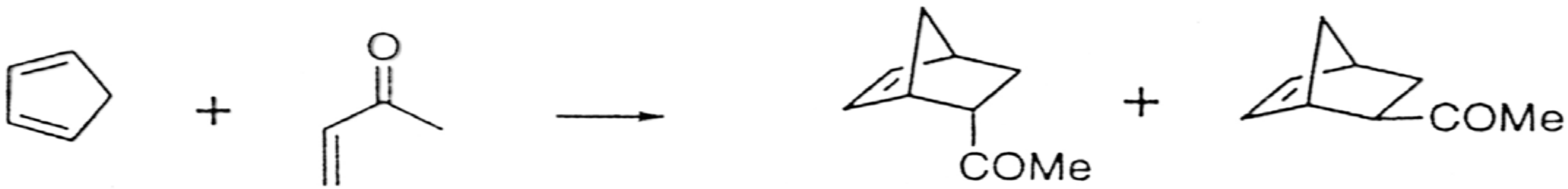


Scheme 5.1 Indium mediated imine coupling

(Adams, p.101)

Diels-Alder Reaction

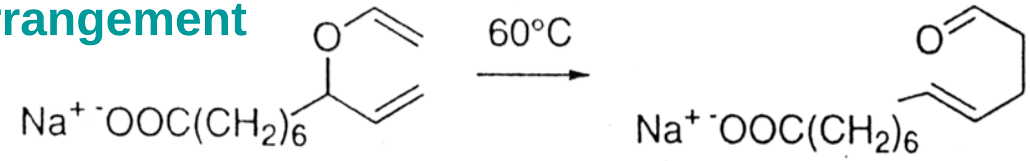
Enhanced Selectivity and Reactivity



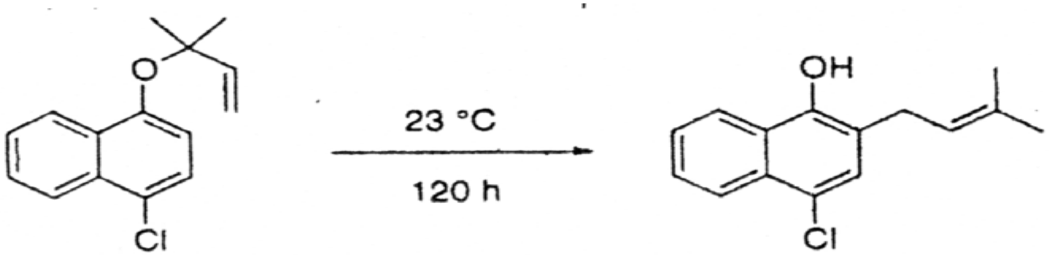
solvent	kinetics 10^5 k ($M^{-1}s^{-1}$)	selectivity endo/exo ratio
isooctane	5.94[a]	
methanol	75.5[a]	8.5[c]
formamide	318[b]	8.9[b]
ethylene glycol	480[b]	10.4[b]
water	4400[a]	25[d]
water (LiCl 4.86 M)	10800[a]	28[d]
water ($(NH_2)_3CCl$ 4.86 M)	4300[a]	22[d]
β-cyclodextrin (10 mM)	10900[a]	
α-cyclodextrin (10 mM)	2610[a]	

Claisen Rearrangement

A sigmatropic rearrangement



solvent	10^{-5} k (s^{-1})
H_2O	18
CF_3CH_2OH	2.6
CH_3OH	0.79



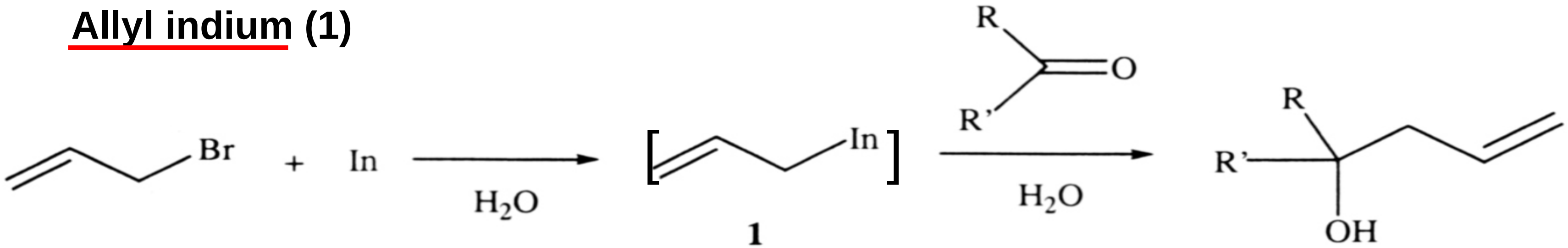
12

13
(m.p.: 54–56 °C)

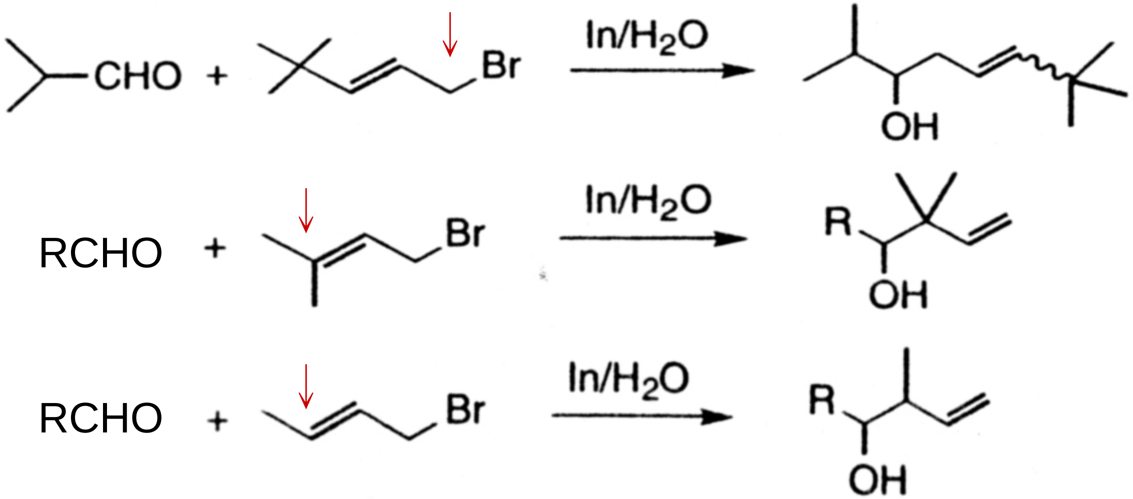
Solvent	Yield [%][b]
toluene	16
DMF	21
CH_3CN	27
MeOH	56[c]
neat	73
on H_2O	**100**

Grignard-type Reactions

Allyl indium (1)

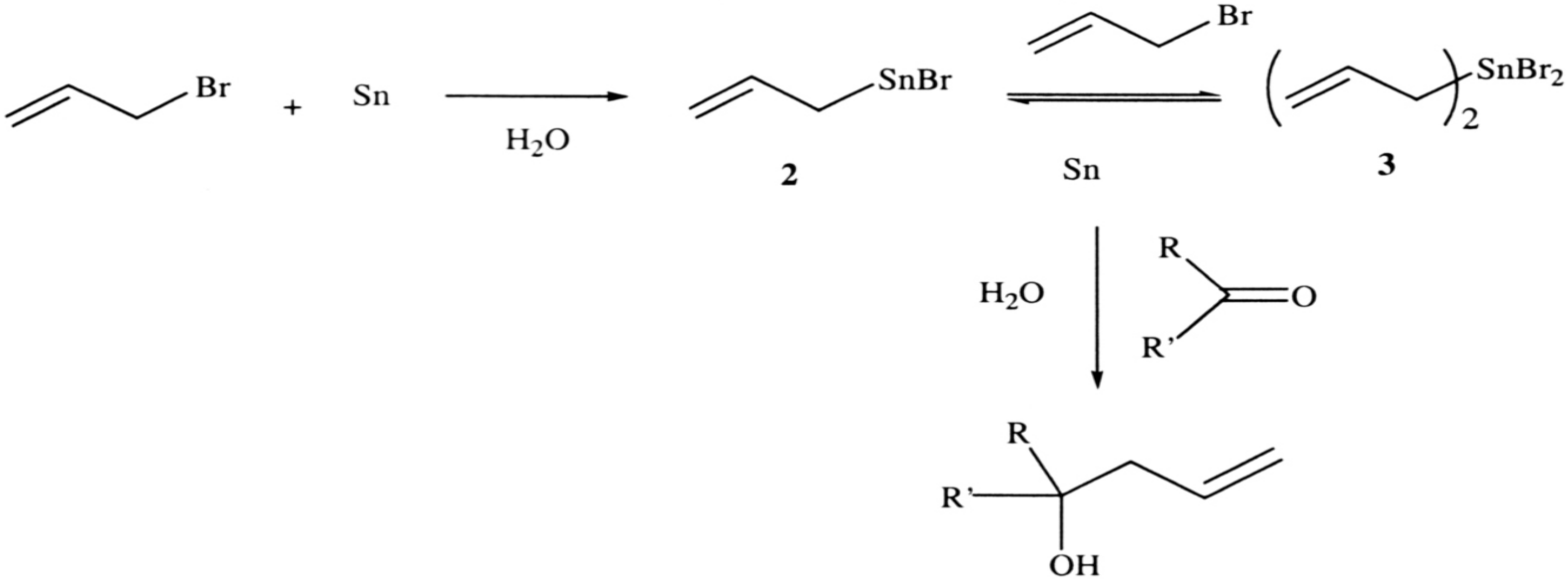


Indium has low first ionization potential (5.70 eV), and is not sensitive to water or base.
The regioselectivity is governed by the bulkiness of the substituent on the C=C.

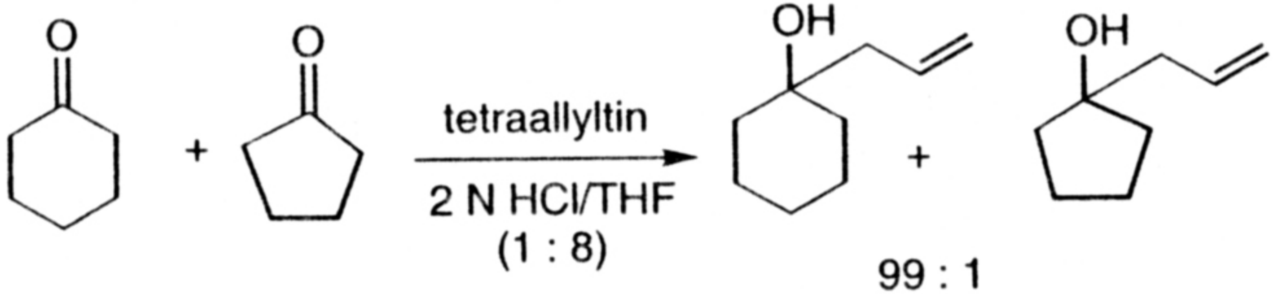


Grignard-type Reactions

Similarly, in the tin-mediated allylation reaction, allyltin intermediates are generated (13). Both allyltin(II) bromide (**2**) and diallyltin(IV) dibromide (**3**) are formed, and can be observed by NMR in the aqueous media (Scheme 3).

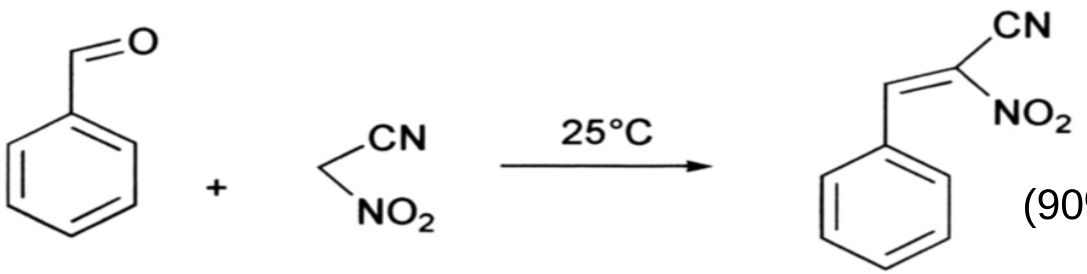


High chemoselectivity



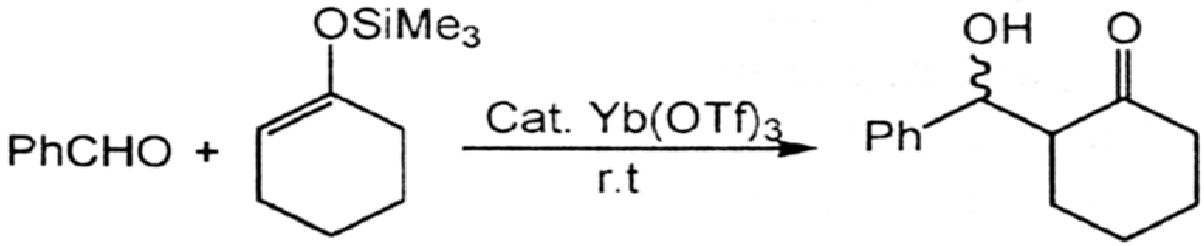
Other C-C bond formations

Condensation of active methylene compounds



(90% yield)

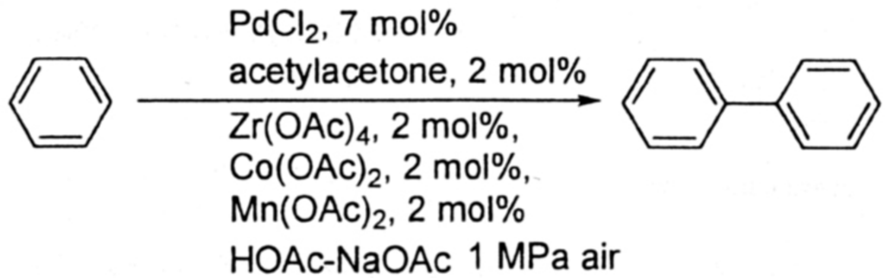
Mukaiyama aldol reactions



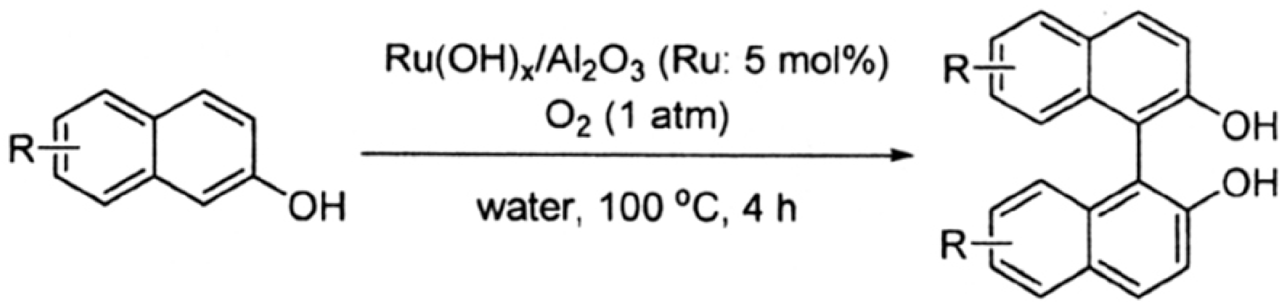
34 35 36

H_2O/THF (1/4)	91%
dry THF	10%

Biaryls



entry	water (mol %)	conversion (%)	selectivity (%)
1	0	96	78
2	250	94	89
3	450	86	91

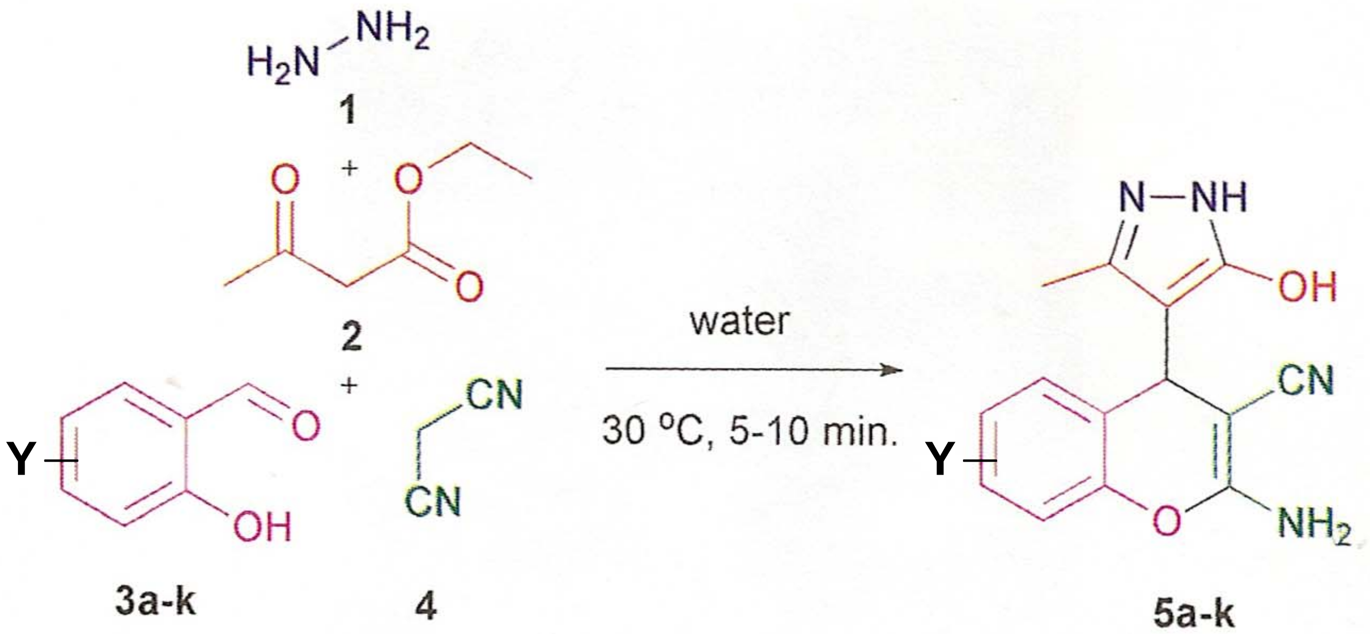


isolated yields: 60-99 %

Four-component catalyst-free reaction in water:

Combinatorial library synthesis of novel 2-amino-4-(5-hydroxy-3-methyl-1*H*-pyrazol-4-yl)-4*H*-chromene-3-carbonitrile derivatives

Kumaravel and Vasuki, *Green Chem.* **2009**, *11*, 1945-1947

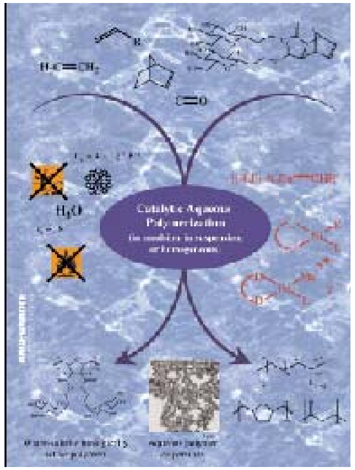


11 Examples

Yield 74-92%

Zhu and Bienaymé (Ed), *Multicomponent Reactions*, 2005, Wiley-VCH

Catalytic Aqueous Polymerization



Mecking, *et al*., *Angew. Chem. Int. Ed.* **2002**, *41*, 545-561

Controlled/'living" radical polymerization applied to water-borne systems

Matyjaszewski, *Macromolecular Symposia*, **2000**, *155*,15-29

Atom Transfer Radical Polymerization employs the activation of an alkyl halide by a transition metal catalyst to for a radical which can initiate polymerization.

Hydrogen atom transfer (HAT) reactions in aqueous media. A mechanistic study

Perchyonok, *et al*., *Green Chem.* **2008**, *10*, 153-163 (C-H formation)

2009 PGCC Academic Award

Atom Transfer Radical Polymerization: Low-impact Polymerization Using a Copper Catalyst and Environmentally Friendly Reducing Agents
Carnegie Mellon University)

Innovation and Benefits: Professor Matyjaszewski (Carnegie Mellon Univ.) developed an alternative process called "Atom Transfer Radical Polymerization (ATRP)" for manufacturing polymers. In ATRP, a Cu(I)-based catalyst, or activator, is continually oxidized to a Cu(II) species during polymerization and replenished by recycling. Activators regenerated by electron transfer (ARGET) reduces the amount of copper catalyst from more than 1,000 ppm to around 1 ppm by using sugar, or ascorbic acid reducing agents. ATRP has been licensed to many manufacturers throughout the world, reducing risks from hazardous chemicals.

(His student Ke Min got 2006 Hancock Memorrial Award for research in ATRP.)

Organic Reactions on Silica in Water

Minakata and Komatsu, *Chem. Rev*. **2009**, *109*, 711-724

Heterogenization of homogeneous catalytic reaction allows for the facile recovery and recycling of catalysts. Two basic approaches have been developed.

1. Immobilization of catalysts on silica supports in a water-only phase.
2. To employ a biphasic system:

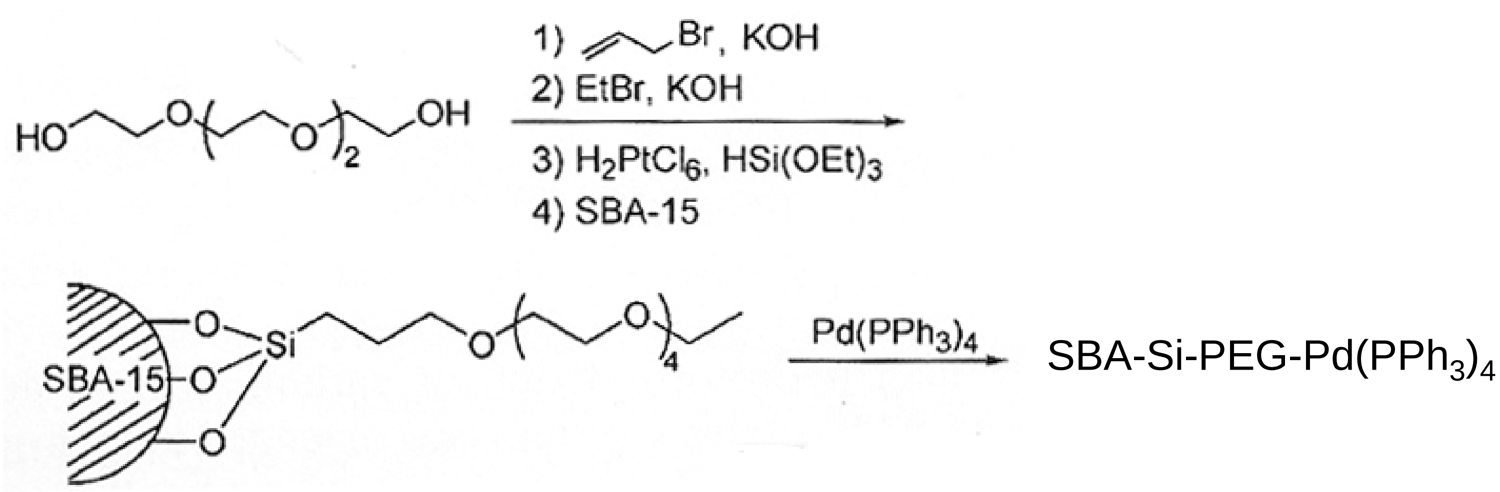
   Water – organic solvent

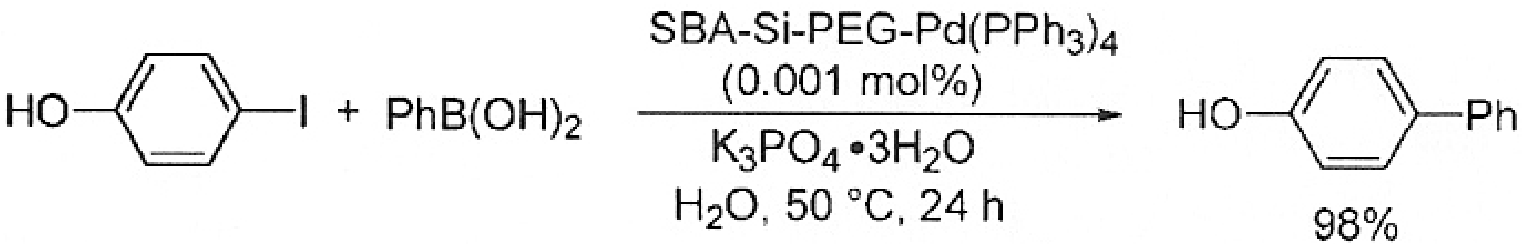
   Water – ionic liquid

   Fluorous reverse-phase silica and water

Silica without modification is also generally used.

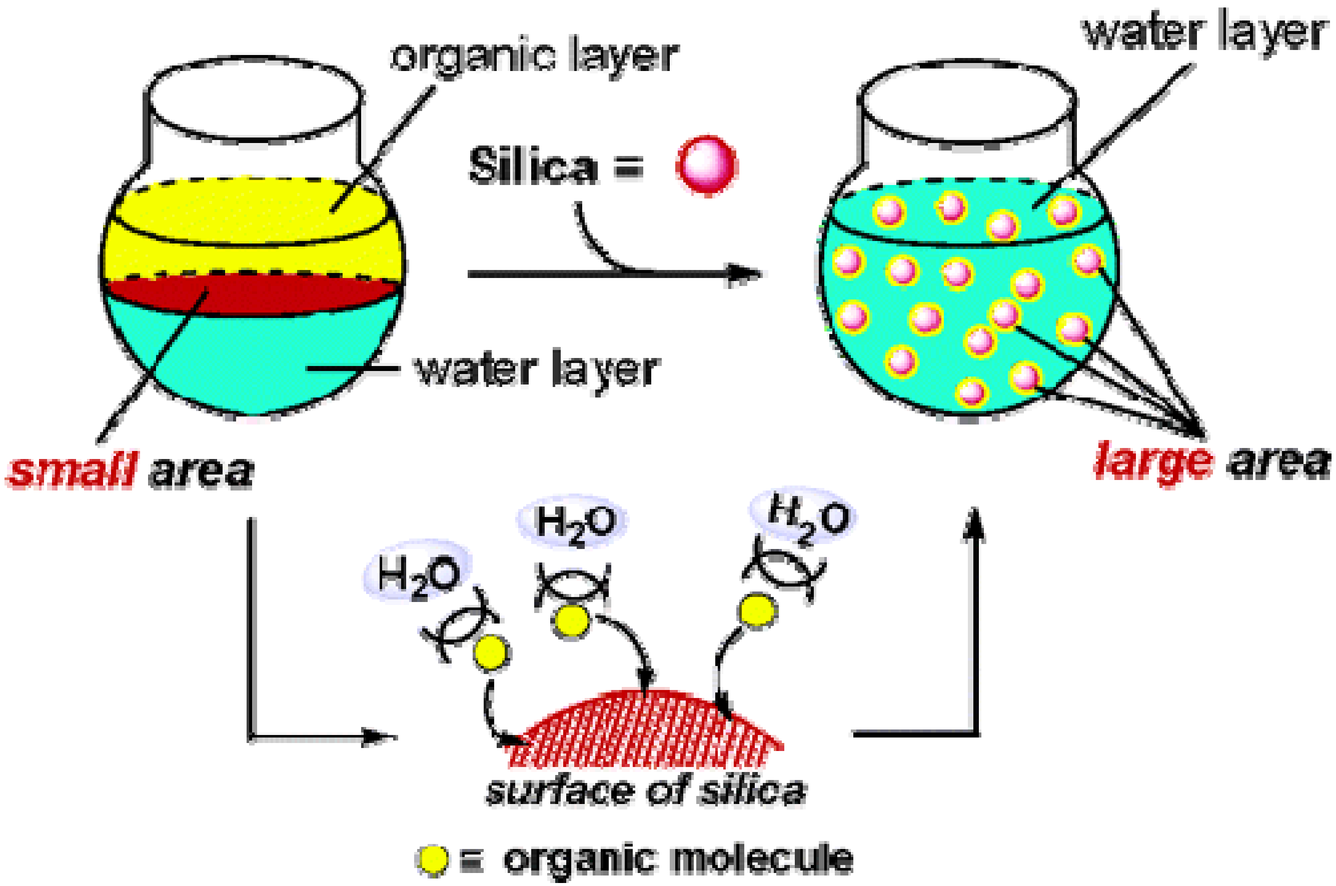
Mesoporous Silica-supported catalyst and Suzuki Coupling



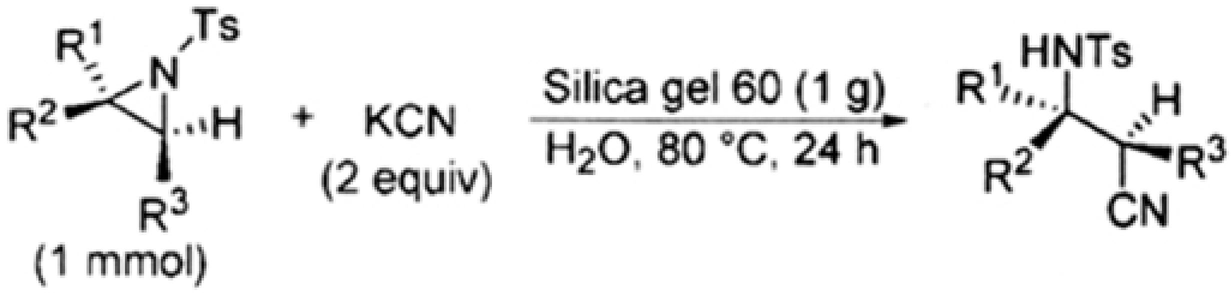


Ring Opening and Expansion of Aziridines in a Silica−Water Reaction Medium

S. Minakata, *et al.*, *J. Org. Chem.*, **2006**, *71* (19), 7471–7472



Ring Opening of Aziridines with KCN

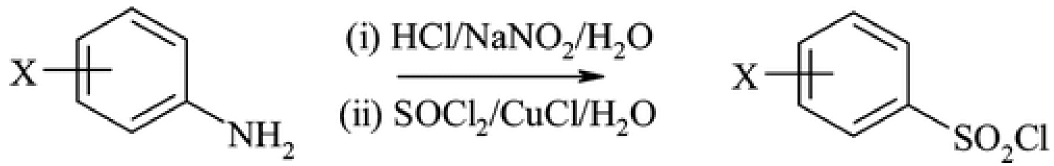


aziridine			
R^1	R^2	R^3	yield (%)
n-C_6H_{13}	H	H	69
CH_2Ph	H	H	72
sec-C_4H_9	H	H	57
Ph	H	H	24
CH_2OH	H	H	32
H	$-(CH_2)_3-$		58
H	$-(CH_2)_4-$		88

Aqueous Process Chemistry

The Preparation of Aryl Sulfonyl Chlorides

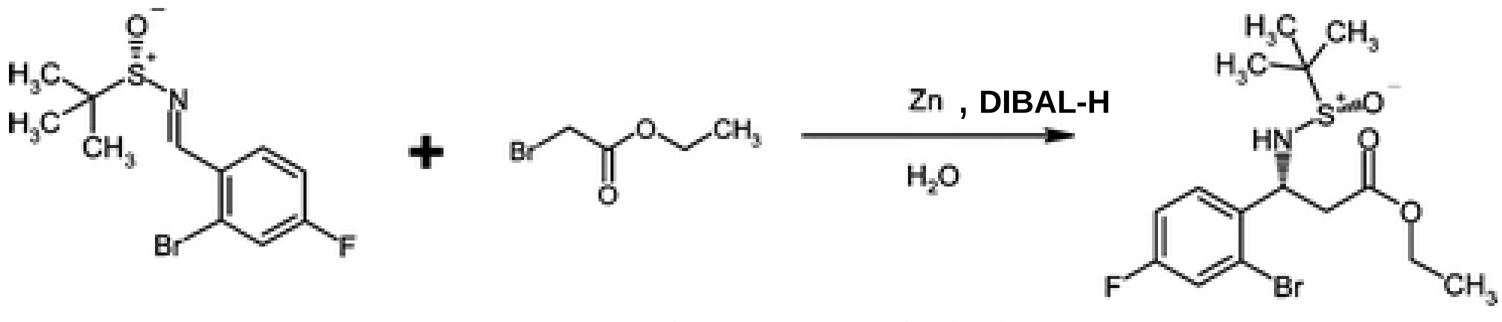
Hogan and Cox, *Org. Proc. Res. Dev.*, **2009**, *13*, 875–879



The method has been shown to be successful for a wide range of electron-deficient and electron-neutral aryl substrates., which results in their direct precipitation from the reaction mixture in >70% yields. **The aqueous process can be readily scaled up and has significant environmental benefits.**

A Scalable Zinc Activation Procedure Using DIBAL-H in a Reformatsky Reaction

Girgis, et al., *Org. Proc. Res. Dev.*, **2009**, *13*, 1094–1099



1 2 3

水資源的消耗

TABLE 13.4 Water Required to Produce Various Materials

Industrial Products	Water Required[a]	Consumer Products	Water Required[b]
Steel 噸	100 噸	Laptop computer	10,600 公升
Paper	20	1 kg flour	77
Copper	400	1 bowl rice	525
Rayon	800	1 L red wine	720
Aluminum	1280	1 cup coffee	140
Synthetic rubber	2400	1 XL cotton tee shirt	30,300

[a]In cubic meters per metric ton. A cubic meter of water weighs 1000 kg, or 1 t.
[b]In liters.

水不應只用一次

Society no longer has the luxury of using water only once.

Levine and Asano, Recovering Sustainable Water from Water Waste, *Environ. Sci. Technol*. **2004**, *38*, 201A-209A

Sustainable Water Award (first in 2010) by RSC

Chemicals from renewable feedstocks

Monographs:

Renewable Resources and Renewable Energy, Ed. M Graziani and P. Fornasiero, CRC Press, **2007**

Catalysis for Renewables, Ed. G. Centi and R. A. van Santen, Wiley-VCH, **2007**

Introduction of Chemicals from Biomass, Ed. J. Clark and F. Deswarte, Wiley, **2008**

Review articles:

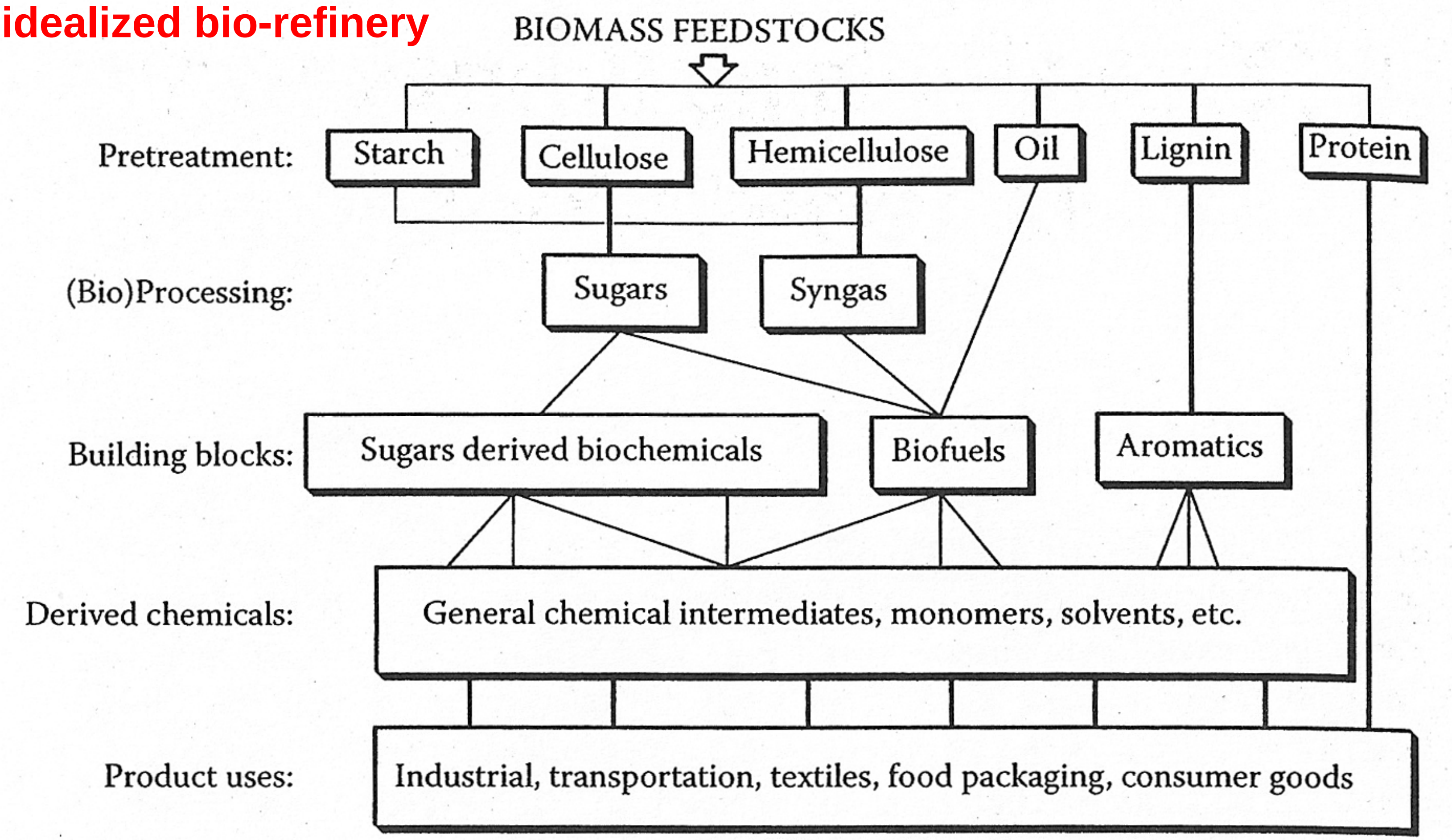
- Corma, et al. *Chem. Rev*. **2007**, *107*, 2411-2502 (general)
- Meier, et al. *Chem. Soc. Rev*. **2007**, *36*, 1788-1802 (polymers)
- Behr, et al. *Green Chem.* **2008**, *10*, 13-30 (glycerol)
- C. Delhomme, et al. Green Chem. **2009**, 11(1),13-26 (succinic acid)

and many more

Renewable resources:

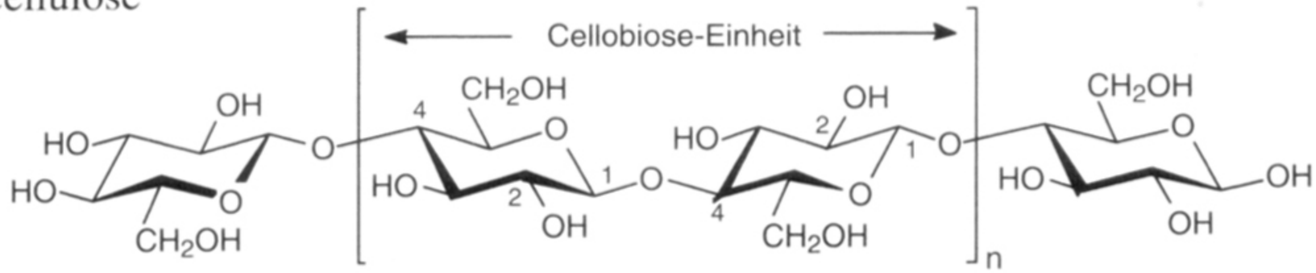
Carbohydrates (sugar, starch, cellulose, etc.), 75%
Lignin, 20%
Fats and oils, proteins, terpenes, etc., 5%

An idealized bio-refinery



Carbohydrates

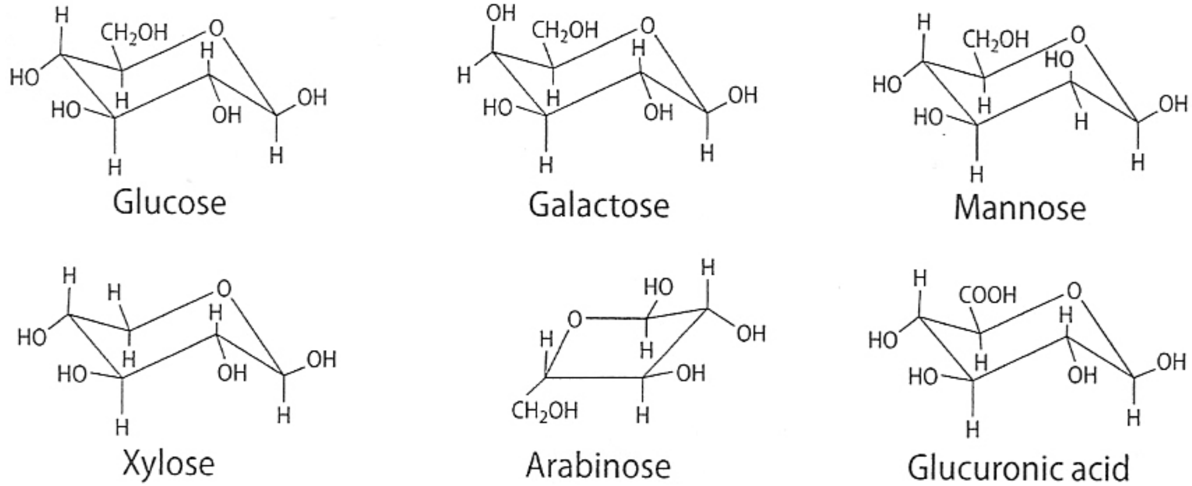
Cellulose



β-1,4'-glycosidic linkage

starch

α-1,4'-glycosidic linkage



Hemicellulose (containing xylose, arabinose, glucose, etc.)

Sucrose (glucose and fructose)

醣類發酵產生乙醇(ethanol)

Chemicals from ethanol

CH_3CH_2OH → $CH_2{=}CH_2$, CH_3CHO, CH_3CO_2H

$CH_2{=}CH_2$ → CH_3CHO → CH_3CO_2H

$CH_2{=}CH_2$ ↓

- Ethyl benzene
- Ethyl bromide
- Ethyl chloride
- Ethylene chlorohydrin
- Ethylene diamine
- Ethylene dibromide
- Ethylene dichloride
- Ethylene glycol
- Ethyleneimine
- Ethylene oxide
- Diethyl ketone
- Diethylene glycol
- Glycol ethers, esters
- MEA, DEA, TEA
- Vinyl acetate
- Polymers, copolymers

CH_3CHO ↓

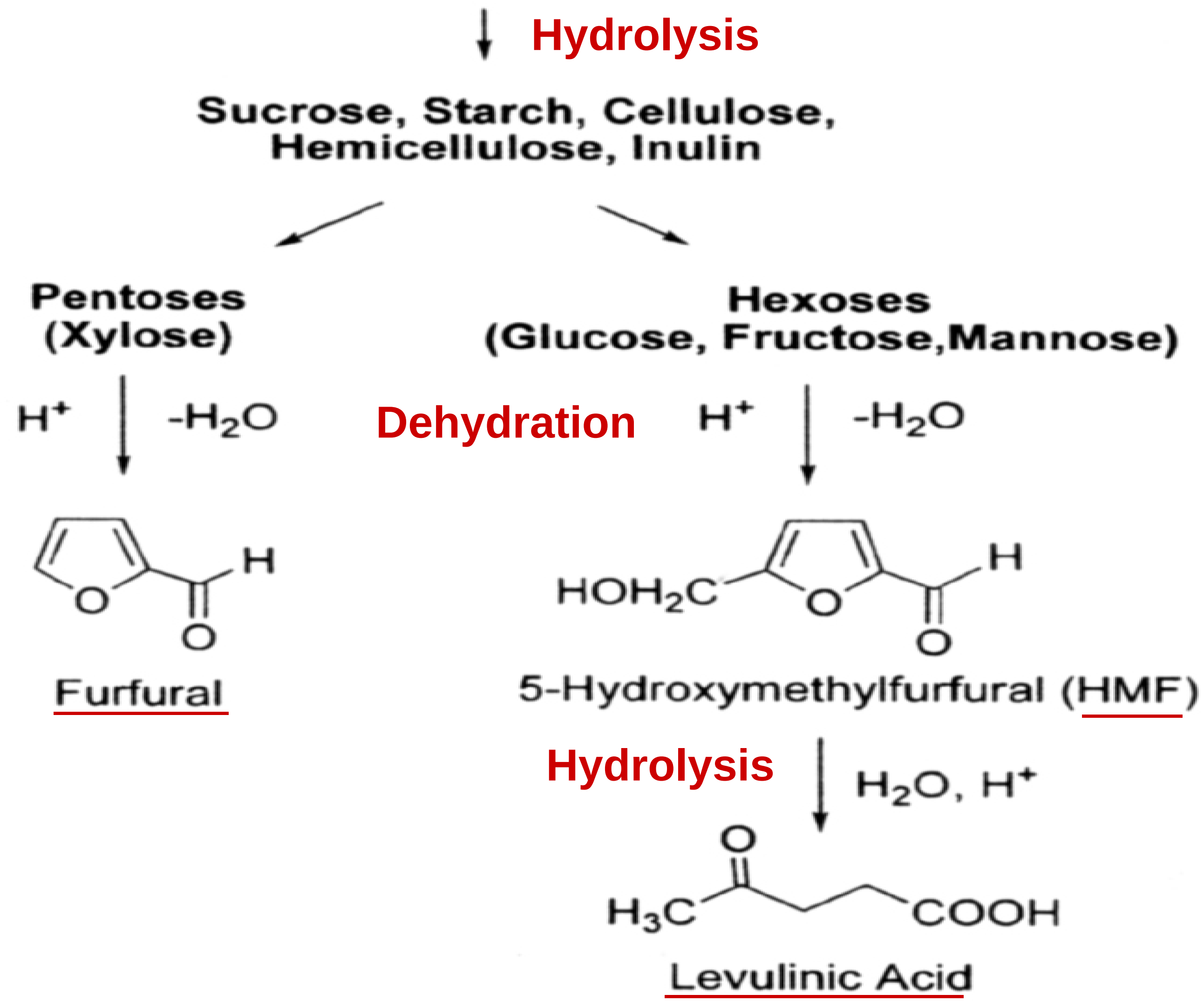
- Acetic acid
- Acetic anhydride
- Aldol products
- Butyl acetate
- Butyl alcohol
- Butyraldehyde
- Chloral
- Ethyleneimine
- Pyridines

CH_3CO_2H ↓

- Acetamide
- Acetanilide
- Acetyl chloride
- Acetic anhydride
- Dimethyl acetamide
- Cellulose acetates
- Esters

如此好資源，為何當燃料？

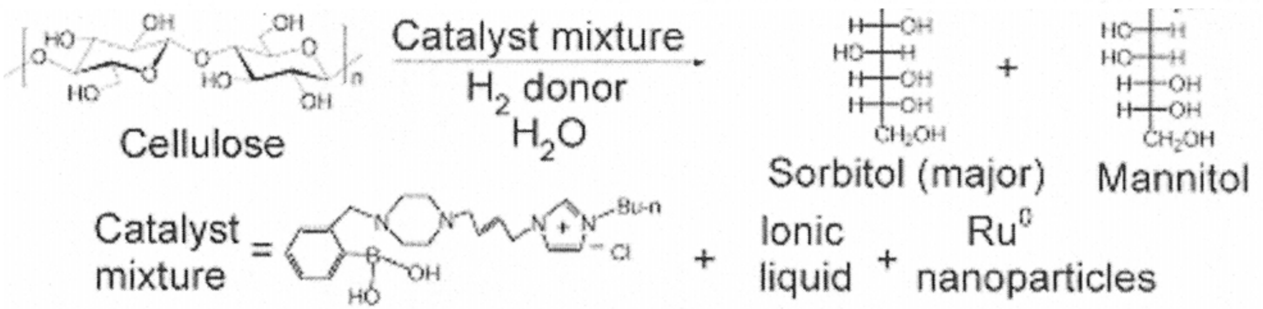
From polysaccharides (vegetal biomass)

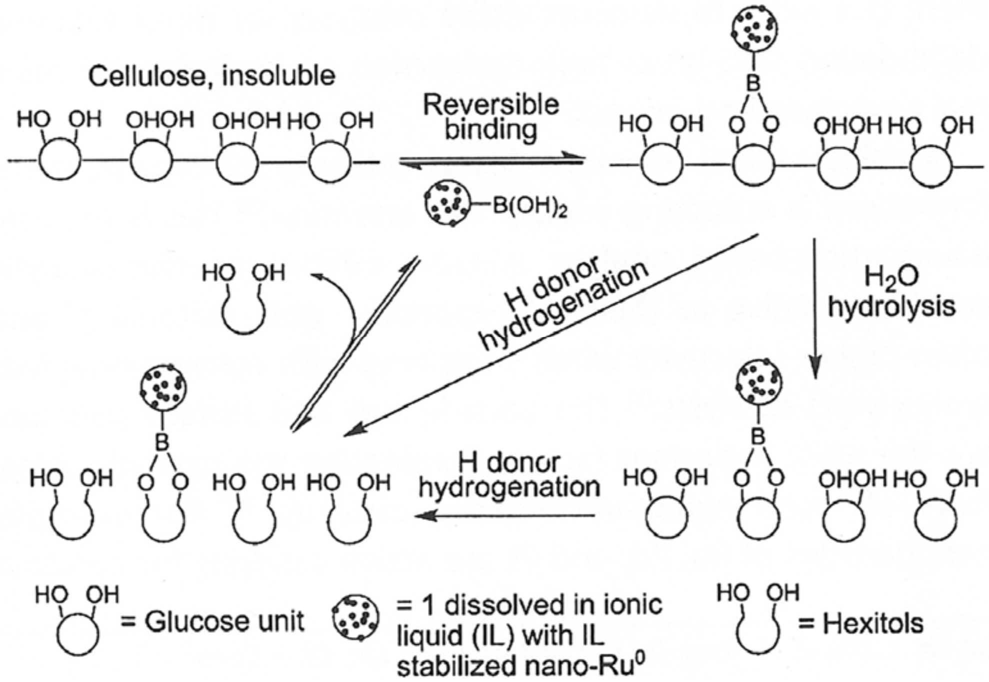


ChemSusChem **2010**, *3*, 67-70

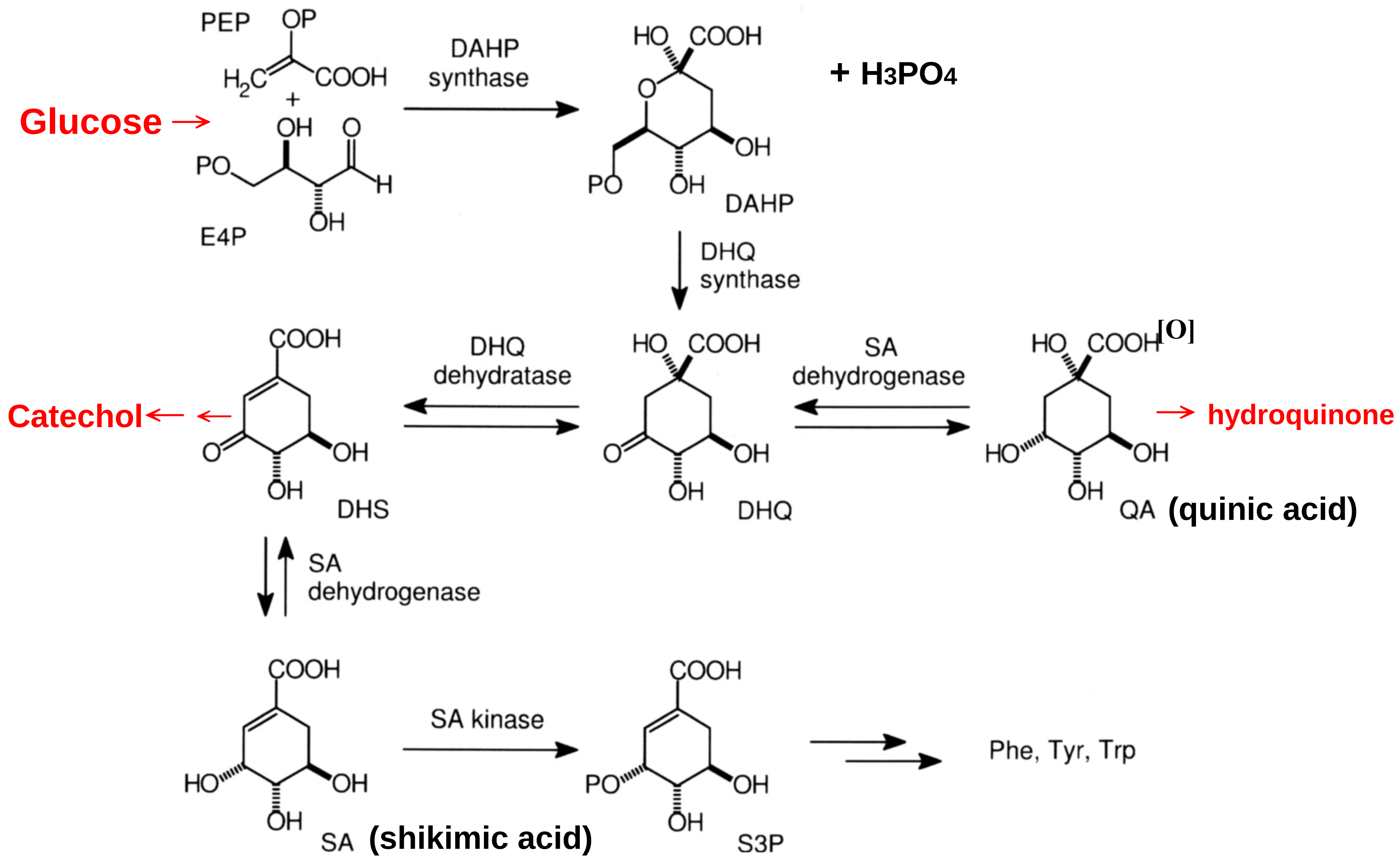
Conversion of Cellulose to Hexitols Catalyzed by Ionic Liquid-Stabilized Ruthenium Nanoparticles and a Reversible Binding Agent

Yinghuai Zhu,*[a] Zhen Ning Kong,[a] Ludger Paul Stubbs,[a] Huang Lin,[a] Shoucang Shen,[a] Eric V. Anslyn,[b] and John A. Maguire[c]



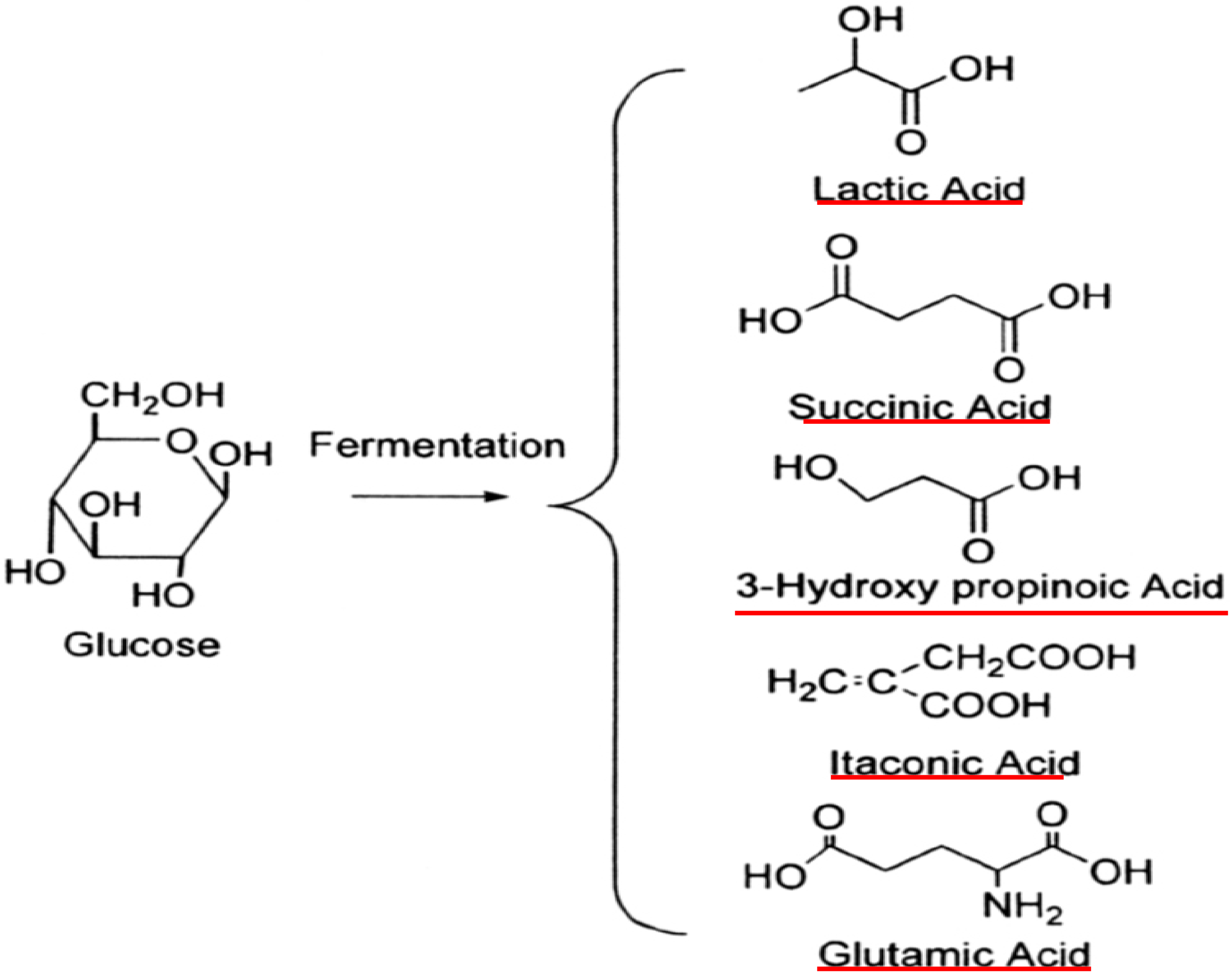


Glucose to other chemicals

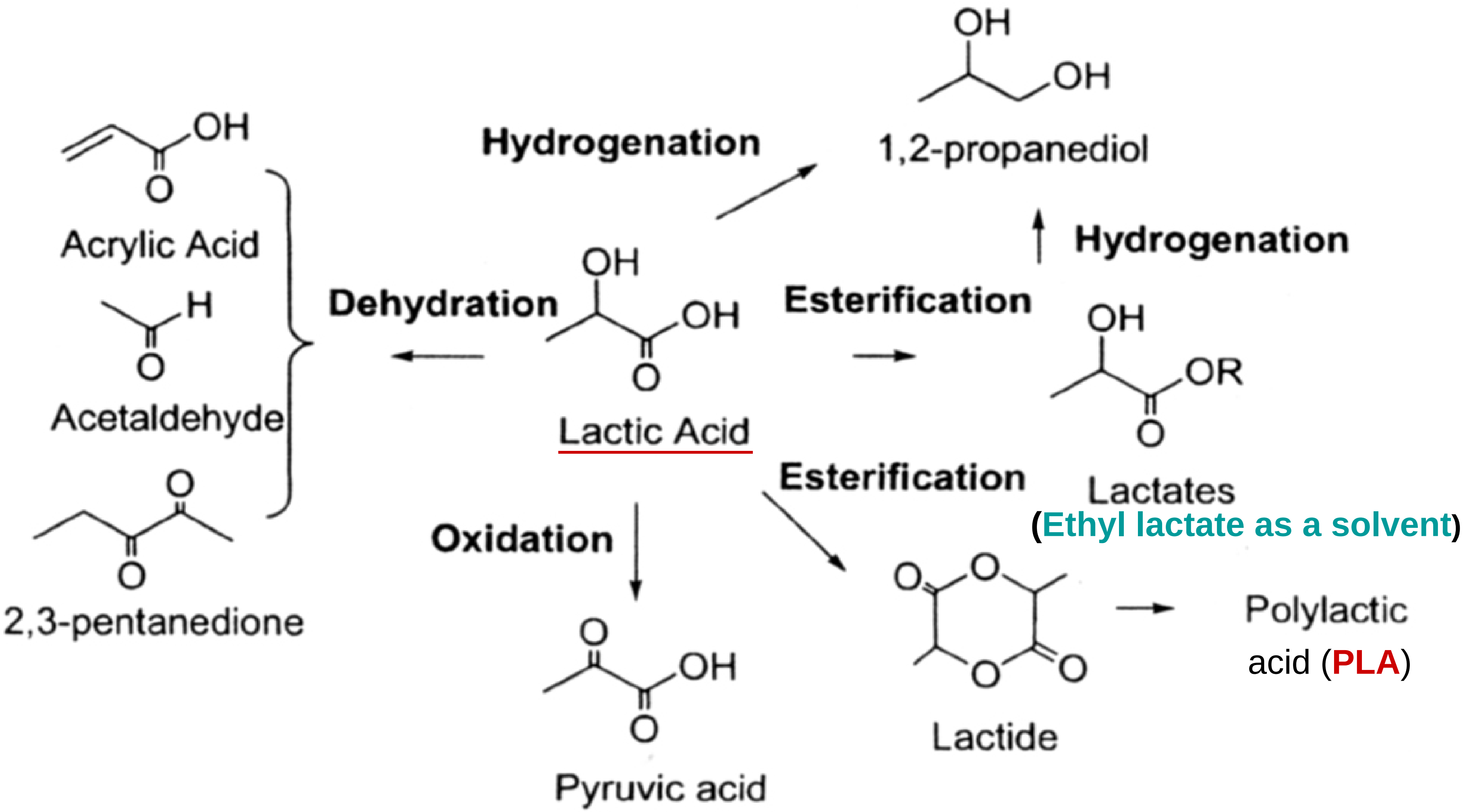


Darths and Frost (MSU), PGCC Award, 1998

More from fermentation of glucose

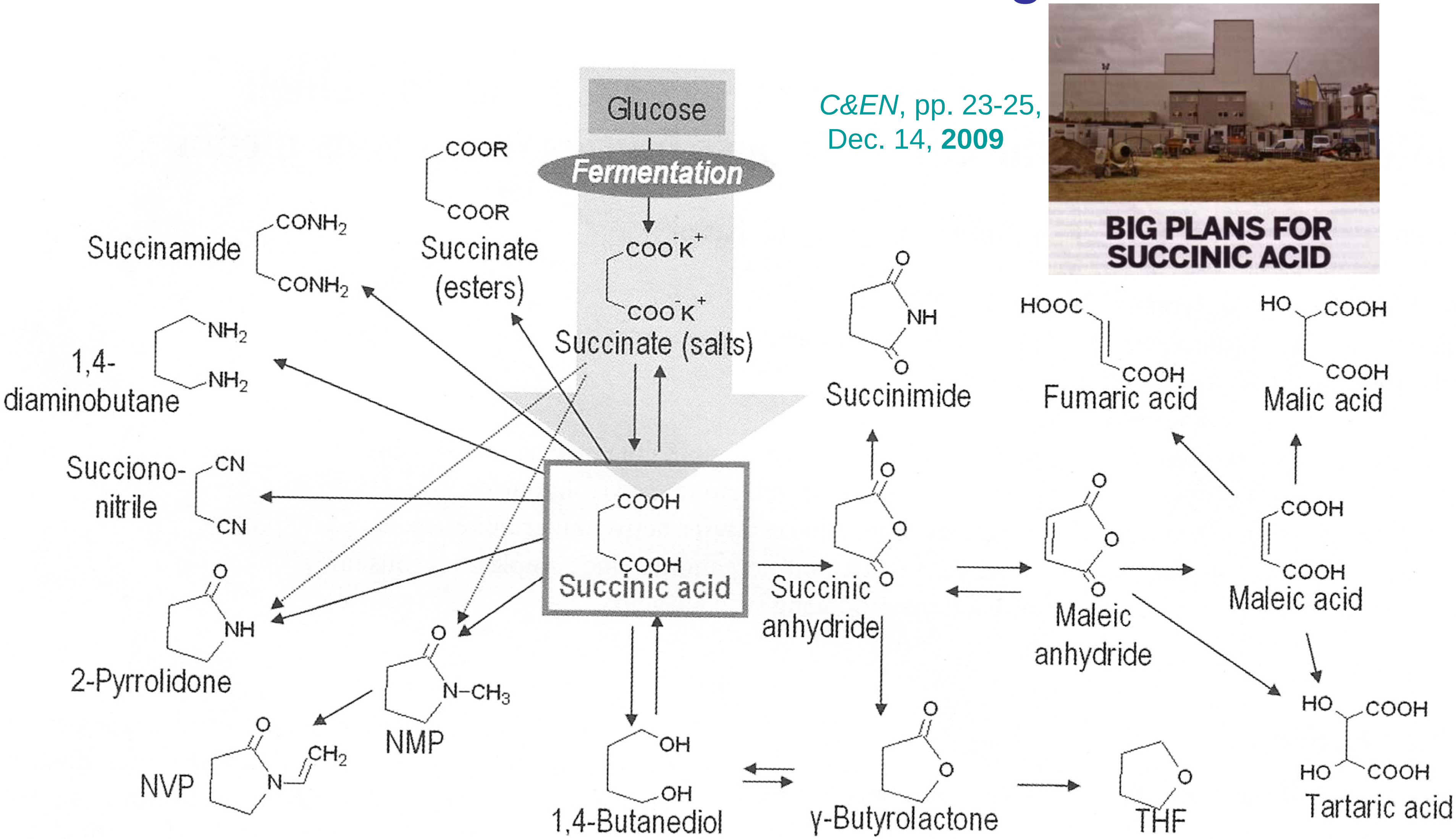


Important chemicals from lactic acid



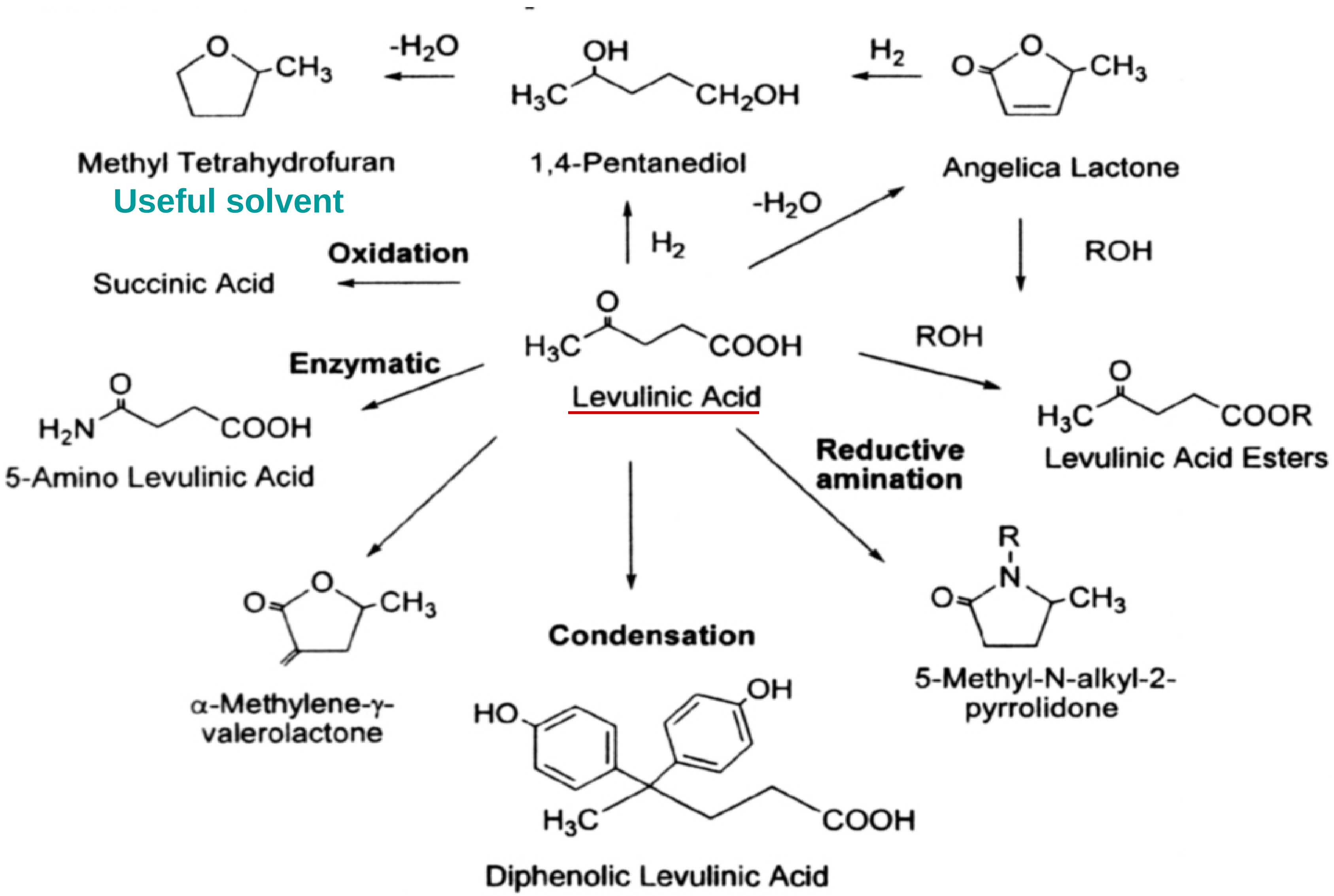
Succinic acid as C-4 building block

C&EN, pp. 23-25, Dec. 14, **2009**



Green Chem. **2009**, *11*, 13-26

Compounds from levulinic acid



1999 PGCC Award of Small Business——Biofine process to make levulinic acid from paper mill sludge, agricultural residues, waste wood and papers.

Inexpensive terpenes to useful chemicals

Limonene

- Limonene is a by-product of the juice industry (50,000 tpa).
- It can be used as a stand alone solvent, and is considered a potential, non-toxic, xylene replacement in some medical applications as it breaks down in the body benign metabolites.
- It can also be dehydrogenated to form *p*-cymene:

p-cymene

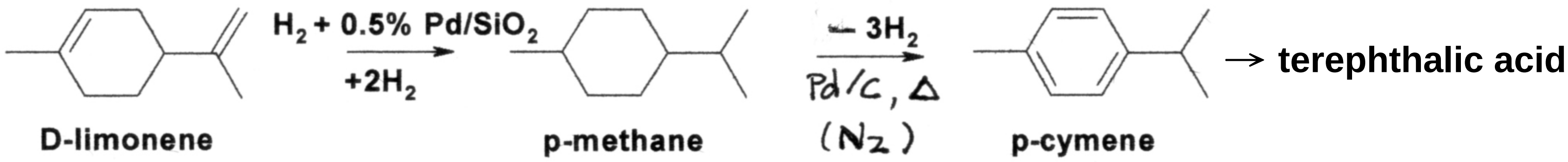
a solvent

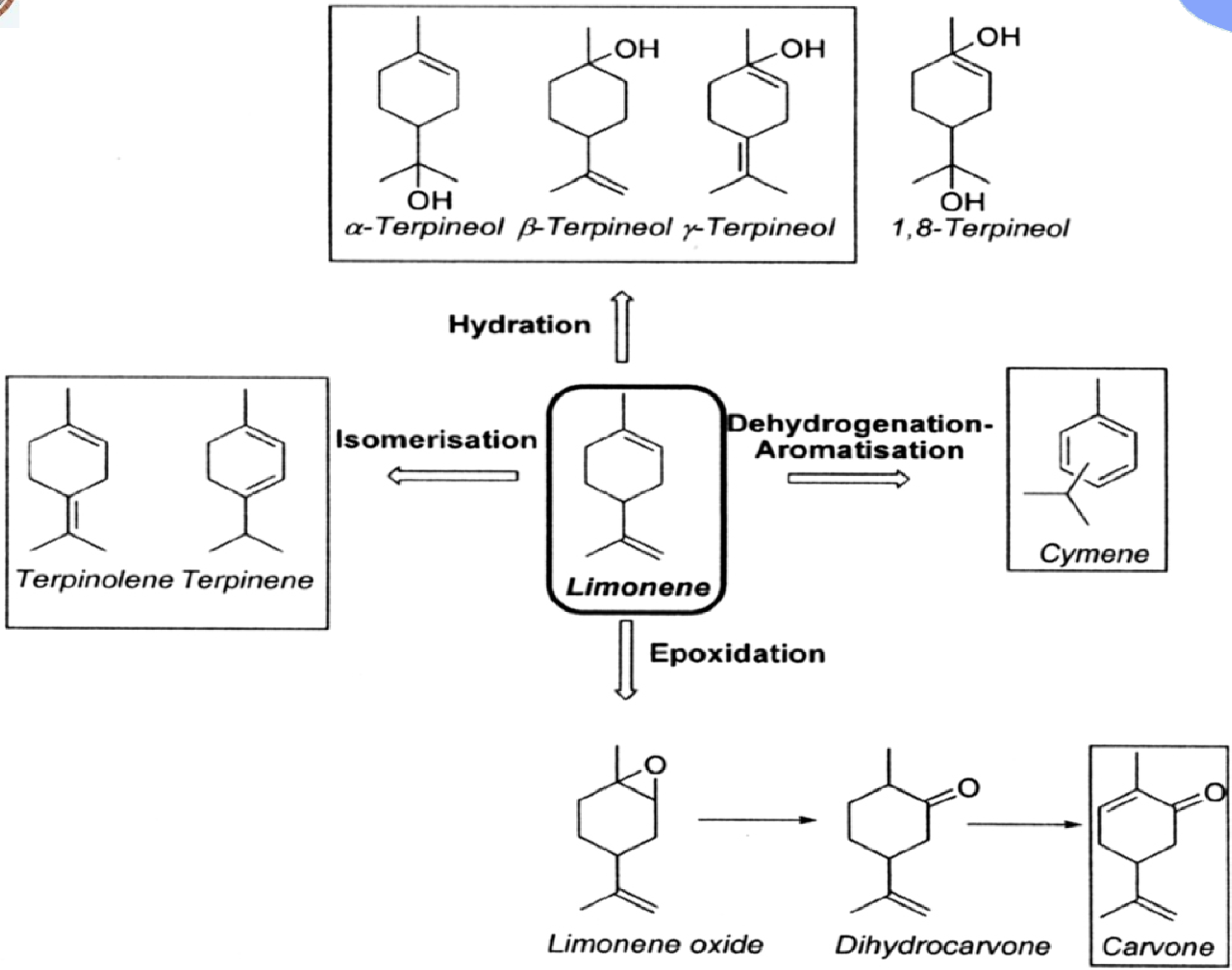
an important intermediate chemical in the fragrance industry

an intermediate

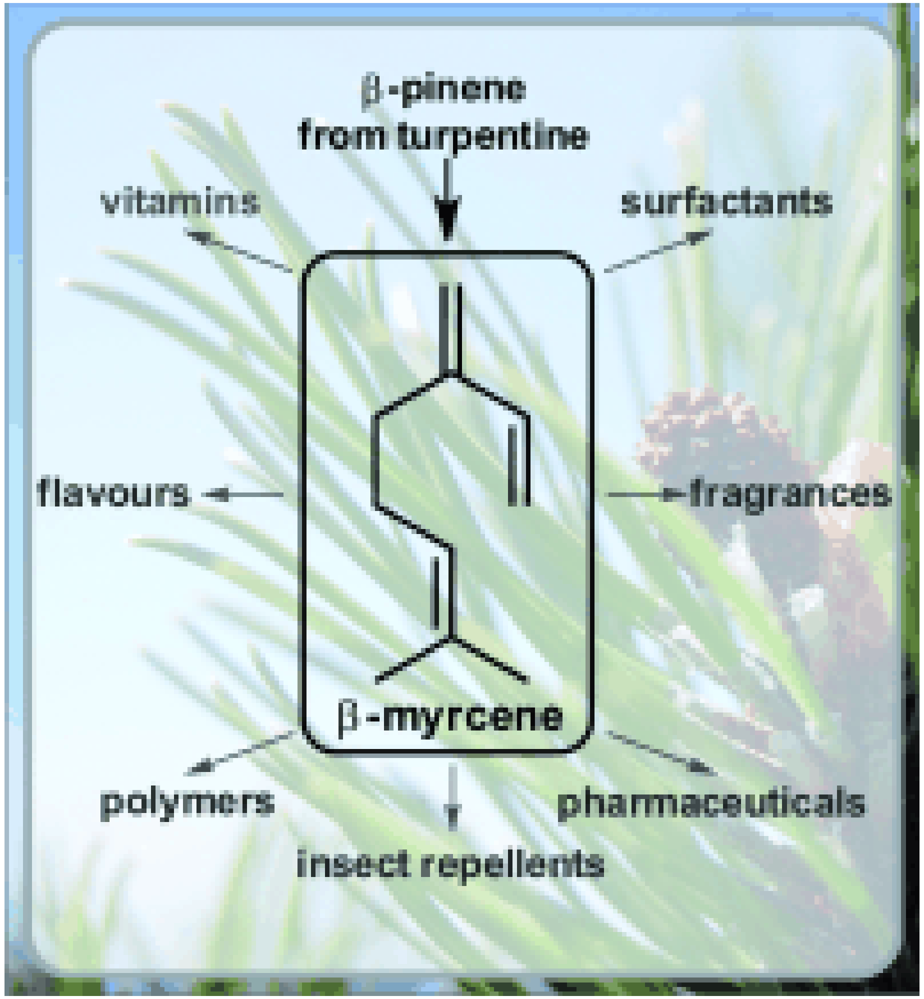
a *p*-cresol intermediate

a raw material for synthesis of non-nitrated musks



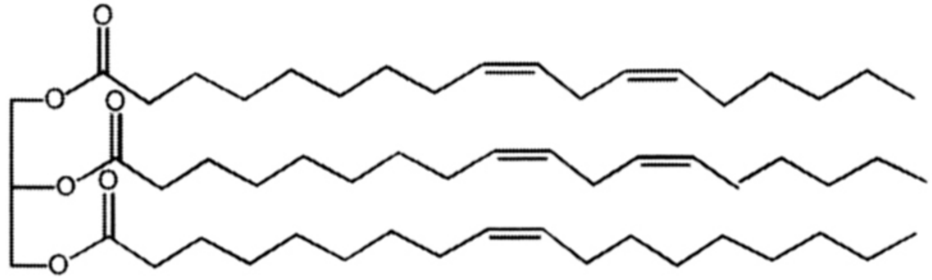

OH
OH
OH
OH
OH
α-Terpineol
β-Terpineol
γ-Terpineol
1,8-Terpineol
Hydration
Isomerisation
Dehydrogenation-
Aromatisation
Terpinolene
Terpinene
Limonene
Cymene
Epoxidation
O
O
O
Limonene oxide
Dihydrocarvone
Carvone

Myrcene as a Natural Base Chemical in Sustainable Chemistry

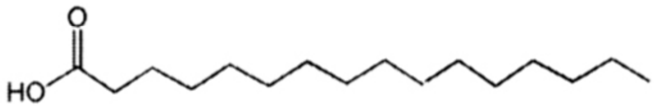


Behr and Johnen, *ChemSusChem* **2009**, *2*, 1072-1095

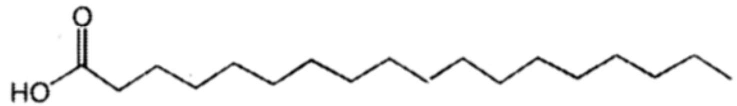
Fats and oils (Triglycerides)



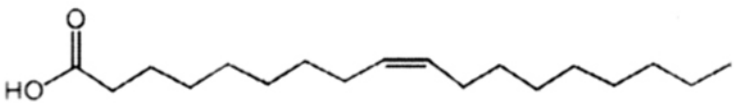
Soybean oil is a statistical mixture of glycerol esters of palmitic acid (10%), stearic acid (3%), oleic acid (23%), linoleic acid (55%), and linolenic acid (9%).



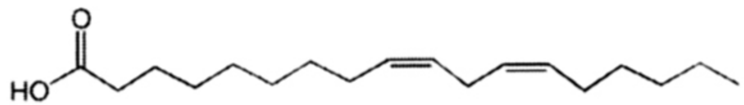
Palmitic acid



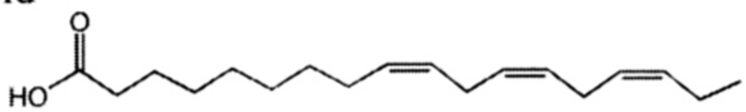
Stearic acid



Oleic acid

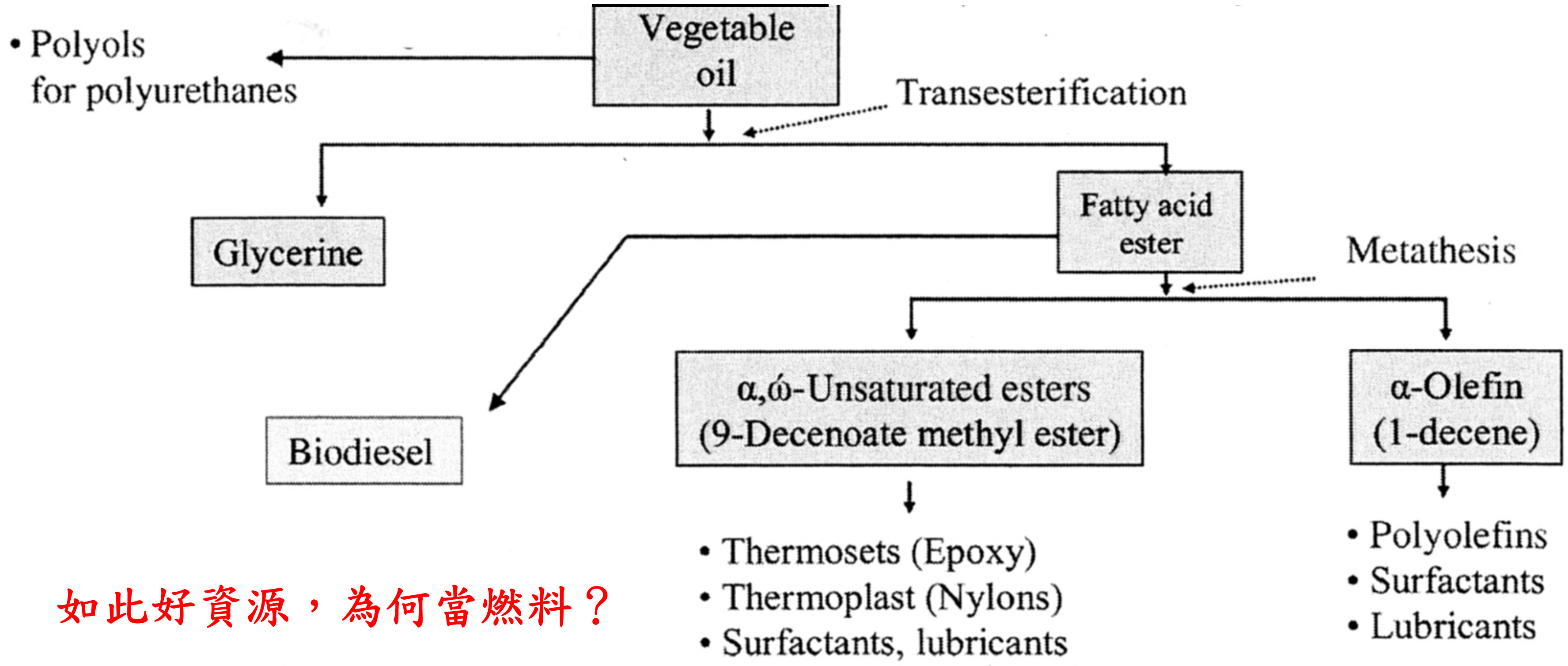


Linoleic acid

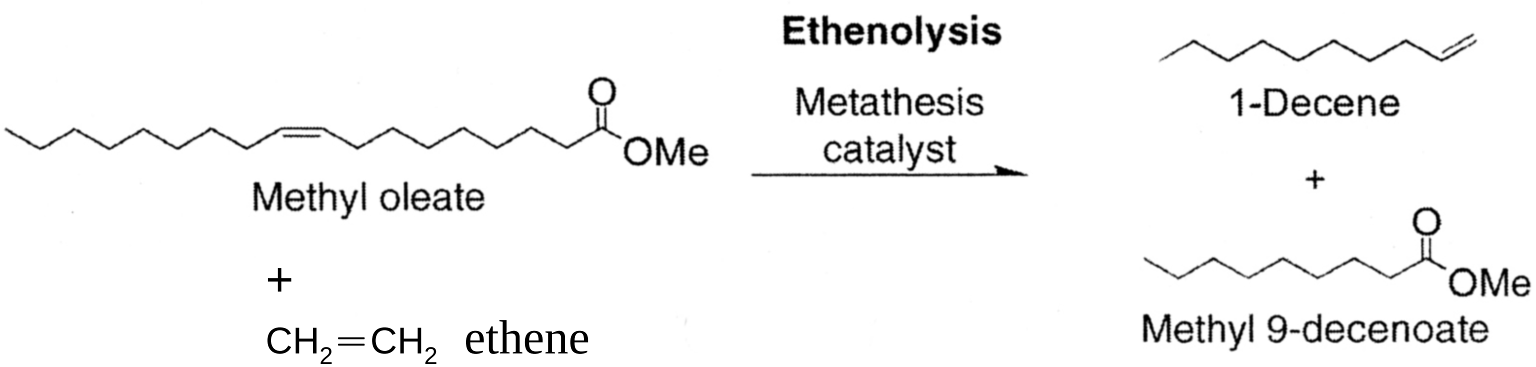


Linolenic acid

Bio-refinery of vegetable oils



如此好資源，為何當燃料？

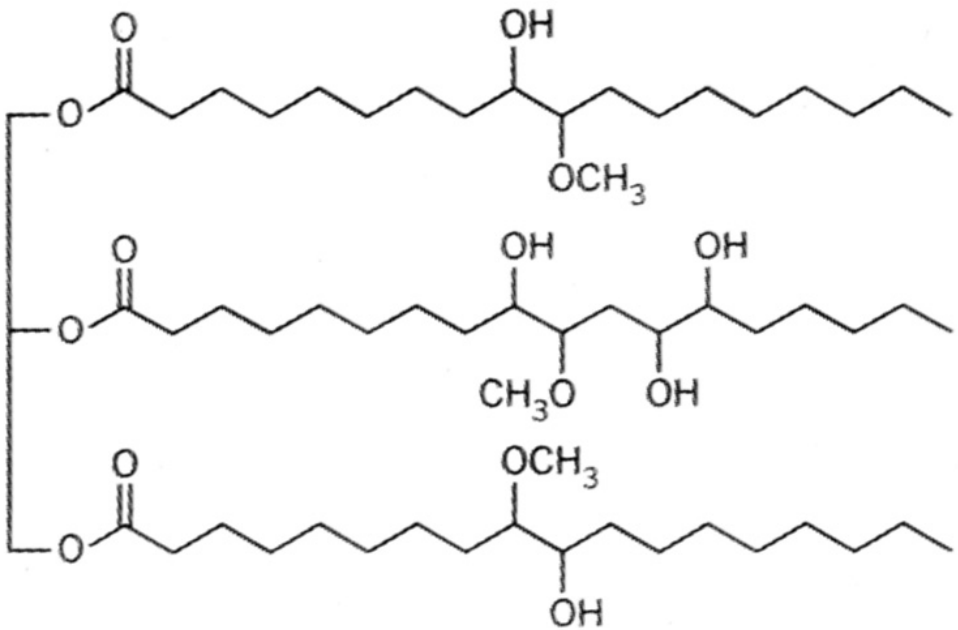


2007 PGCC Designing Greener Chemicals Award

BiOH™ Polyols

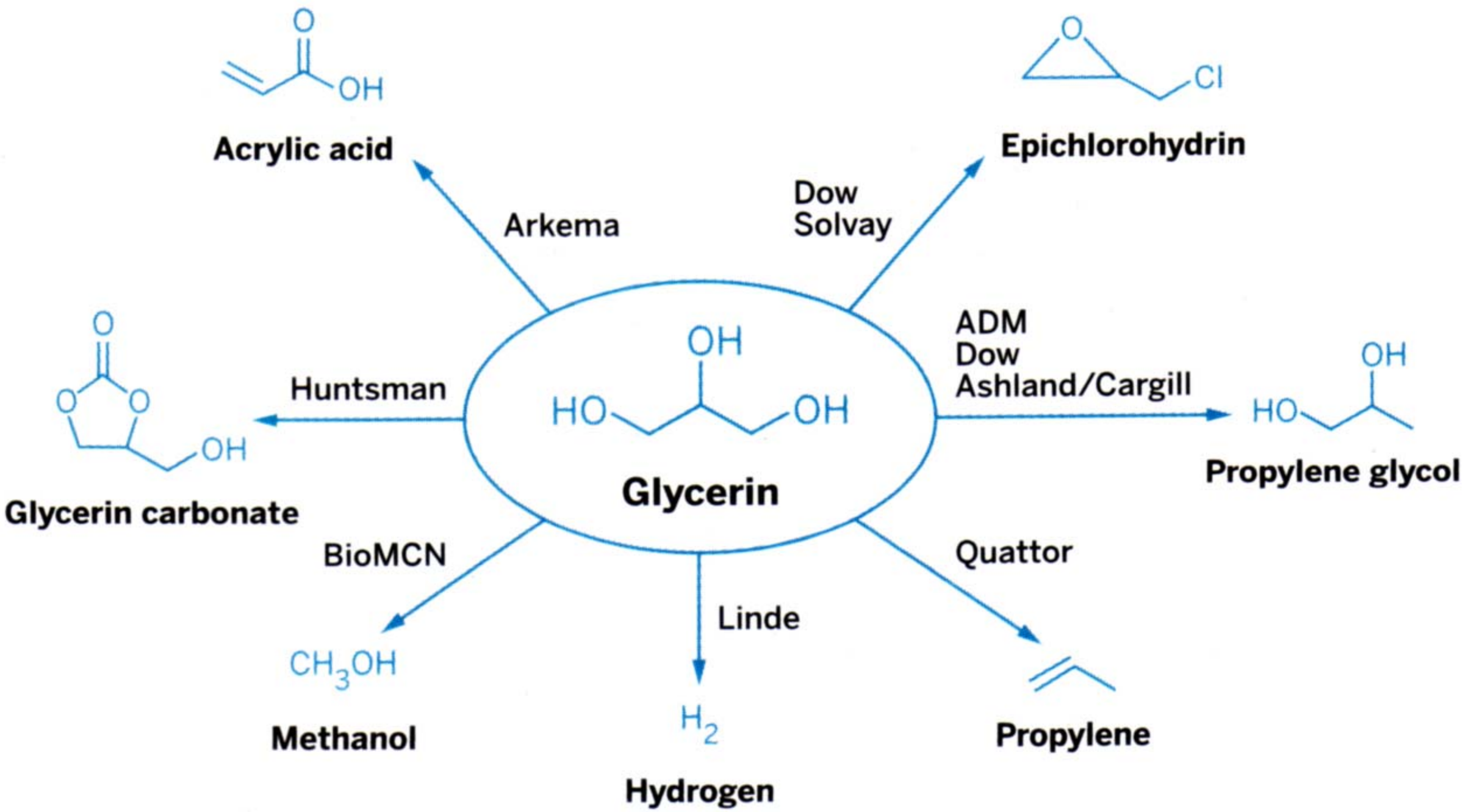
Cargill, Incorporated

Innovation and Benefits: One of the two chemical building blocks used to make polyurethane is a "polyol." Polyols are conventionally manufactured from petroleum products. Cargill's BiOH™ polyols are manufactured from renewable sources such as soybean oils. Each million pounds of BiOH™ polyols saves nearly 700,000 pounds of crude oil. Cargill's process reduces total energy use by 23 % and carbon dioxide emissions by 36 %.

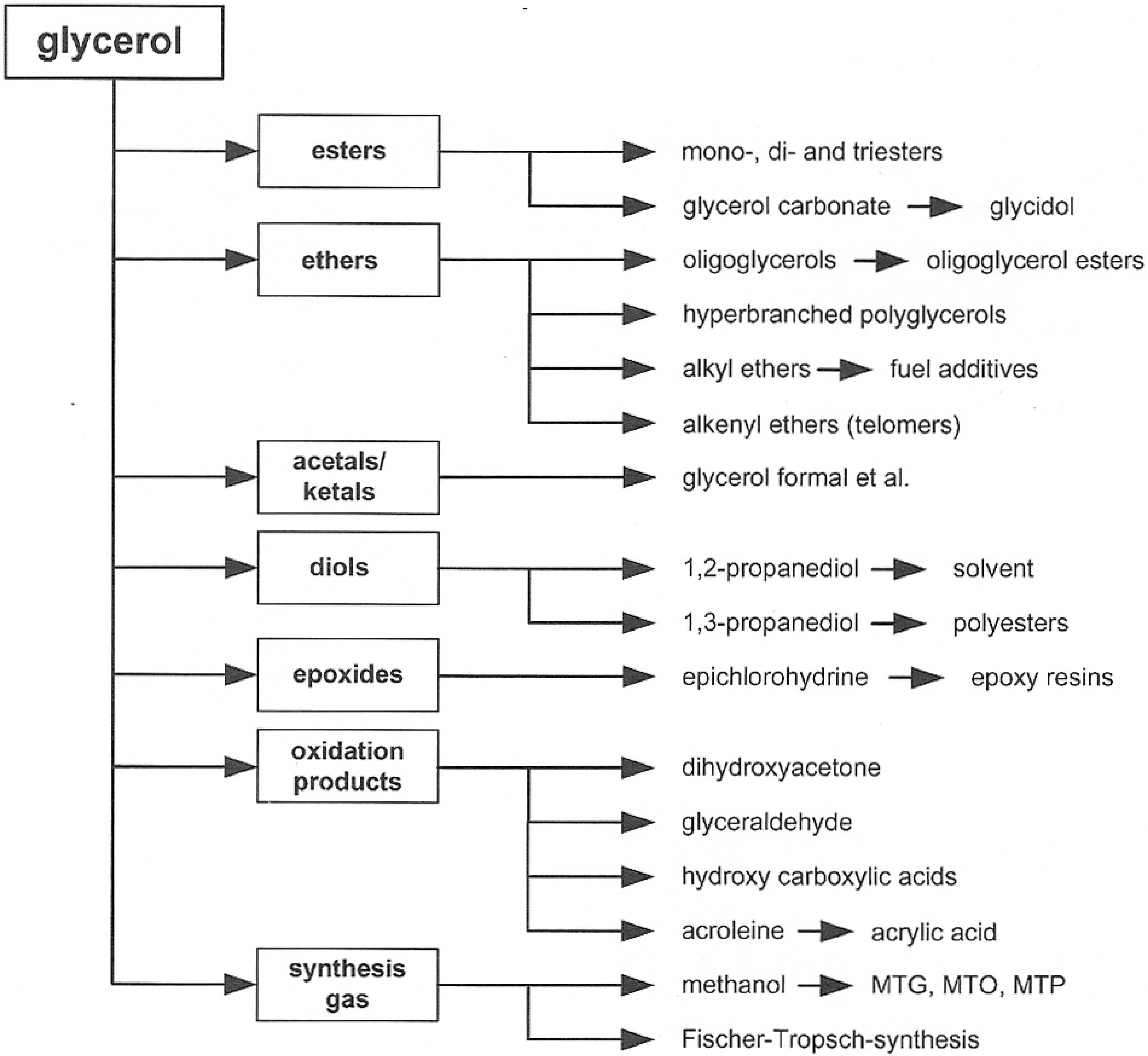


The use of fatty acids and glycerol

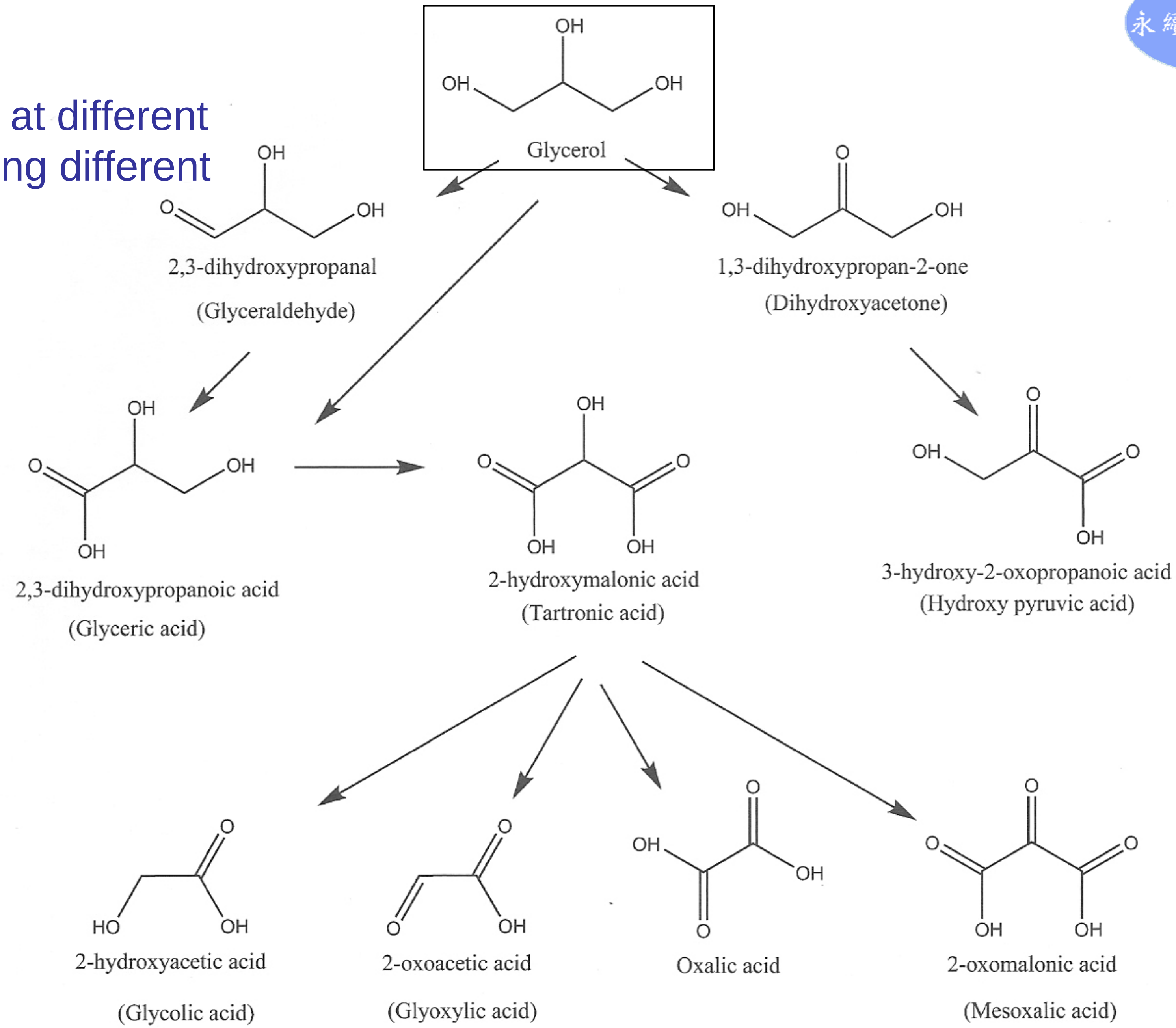
- The acidic function (COOH) can be modified.
- The alkene function (C=C) can be modified.
- Glycerol (glycerin) is a potentially versatile feedstock.



(C&EN, pp. 16-17, June 16 , 2009)


glycerol
esters
mono-, di- and triesters
glycerol carbonate
glycidol
ethers
oligoglycerols
oligoglycerol esters
hyperbranched polyglycerols
alkyl ethers
fuel additives
alkenyl ethers (telomers)
acetals/ ketals
glycerol formal et al.
diols
1,2-propanediol
solvent
1,3-propanediol
polyesters
epoxides
epichlorohydrine
epoxy resins
oxidation products
dihydroxyacetone
glyceraldehyde
hydroxy carboxylic acids
acroleine
acrylic acid
synthesis gas
methanol
MTG, MTO, MTP
Fischer-Tropsch-synthesis

Oxidation at different pH, or using different oxidant



2003 Greener Reaction Conditions Award

Microbial Production of 1,3-Propanediol

Innovation and Benefits:

DuPont **and Genencor International jointly developed a genetically engineered microorganism to manufacture the key building block for DuPont's Sorona® polyester. This achievement, comprising biocatalytic production of 1,3-propanediol from renewable resources, offers economic as well as environmental advantages… (**glucose → glycerol → 1,3-propanediol**)**

2006 Academic Award

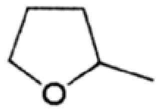
Biobased Propylene Glycol and Monomers from Natural Glycerin

Innovation and Benefits:

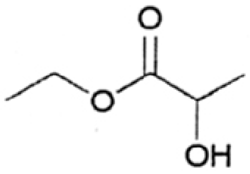
Professor Suppes **(U. Missori-Columbia) developed an inexpensive method to convert waste glycerin, a byproduct of biodiesel fuel production, into propylene glycol, which can replace ethylene glycol in automotive antifreeze. It can help biodiesel become a cost-effective, viable alternative fuel…**

(glycerol → 1,2-propanediol**)**

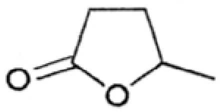
Solvents from renewable resources



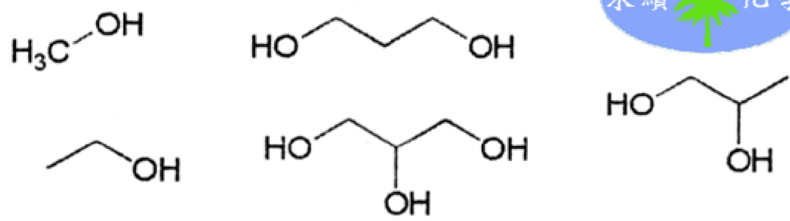
2-MeTHF



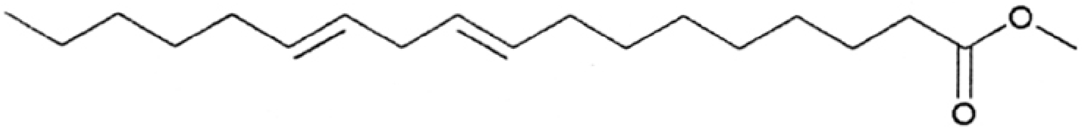
Ethyl lactate



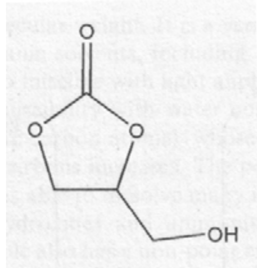
γ -Valerolactone



Alcohols and polyols



Fatty acid ester (Biodiesel component)



Glycerol carbonate

Industrial uses of esteric green solvents

Solvent	*Industrial use*
Glycerol carbonate	Non-reactive diluent in epoxy or polyurethane systems
Ethyl lactate	Degreaser
	Photo-resist carrier solvent
	Clean-up solvent in microelectronics and semiconductor manufacture
2-Ethylhexyl lactate	Degreaser
	Agrochemical formulations
Fatty acid esters (and related compounds)	Biodegradable carrier oil for green inks
	Coalescent for decorative paint systems
	Agrochemical/pesticide formulations

敬請不吝指教

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