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。[如本頁取材自〇〇〇教授演講內容]。

永續化學合成(4)

可再生性資源在合成上的利用

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(Revised May 6, 2010)

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

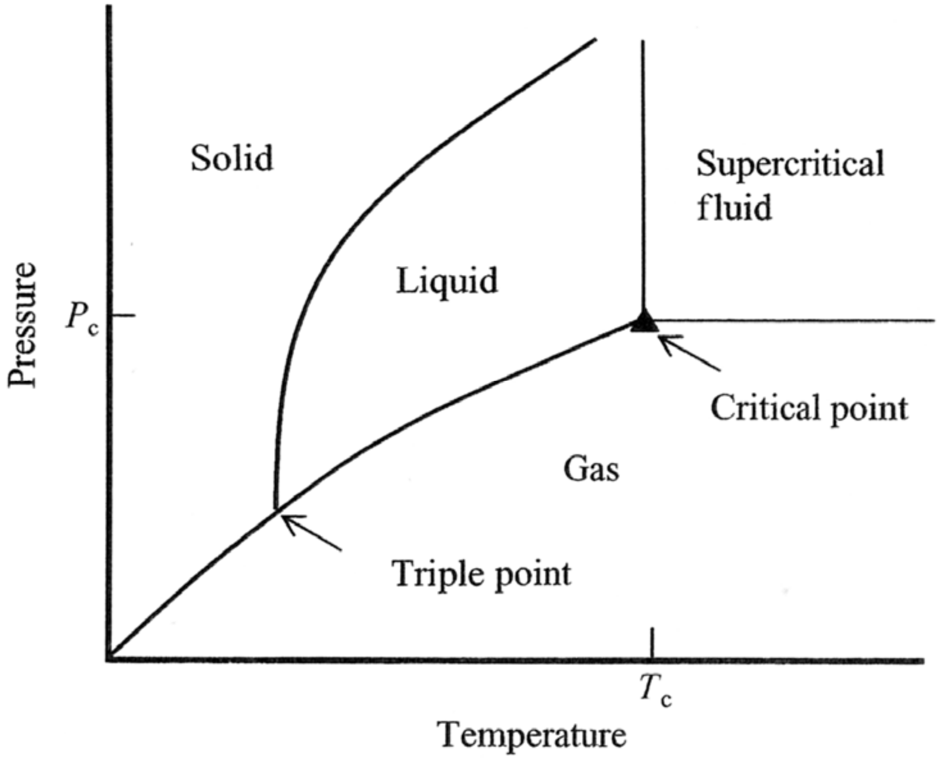
Green Chemistry Using Liquid and Supercritical Carbon Dioxide (DeSimone and Tumas, Ed., Oxford, **2003**)

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 or a reagent

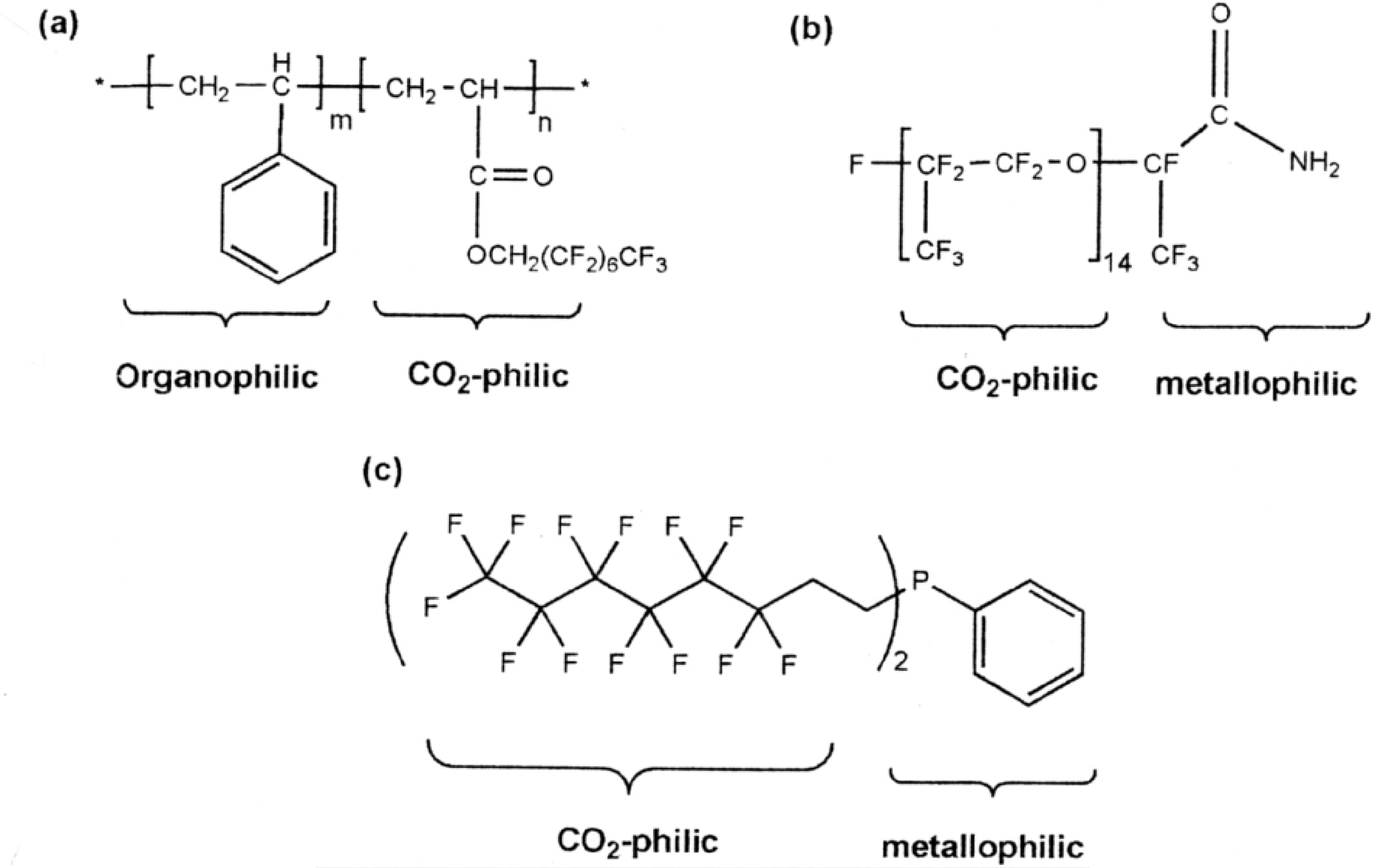
Advantages	*Disadvantages*
Non-toxic	Relatively high pressure equipment
Easily removed	Equipment can be capital intensive
Potentially recyclable	Relatively poor solvent
Non-flammable	Reactive with powerful nucleophiles
High gas solubility	Possible heat-transfer problems
Weak solvation	
High diffusion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

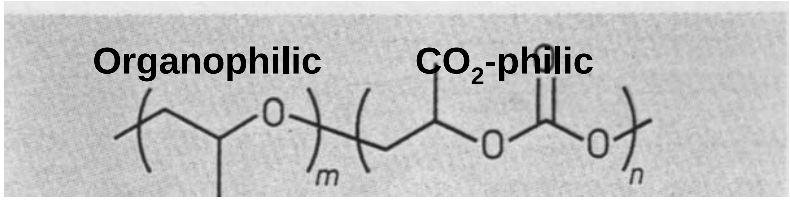
(Lancaster, *Green Chemistry* Table 5.3)

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

Surfactants for SCF-CO_2

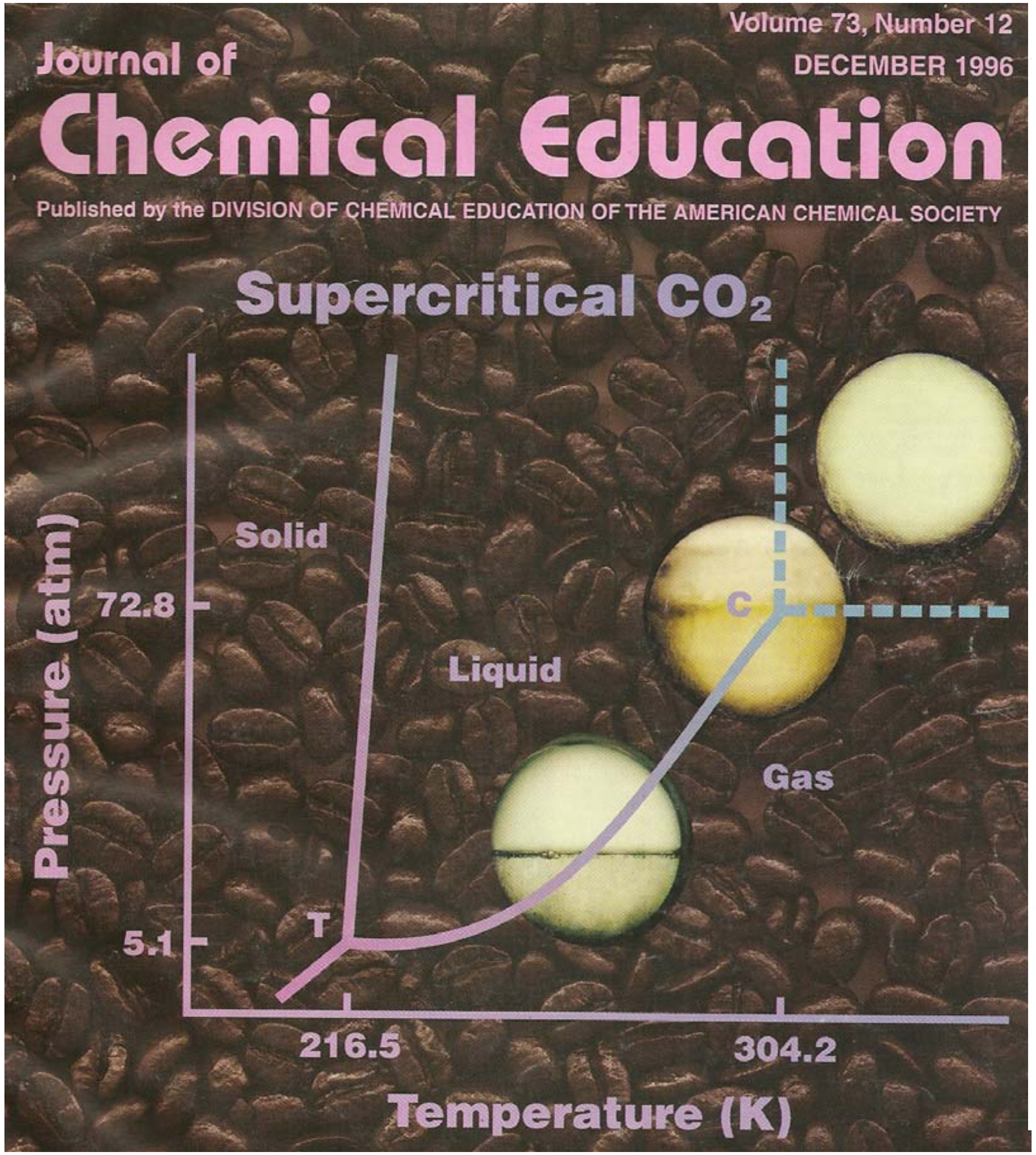




Non-fluorinated (ether-carbonate) copolymer by Beckman and coworkers at U. of Pittsburgh. **PGCC Award of 2002**

(*J. Phys. Chem. B*, **2009**, *113*, 14971-14980)

“老” 技術



Chemical reactions in supercritical carbon dioxide
C. M. Wai, *J. Chem. Educ*. **1996**, *75*, 1641-1645

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

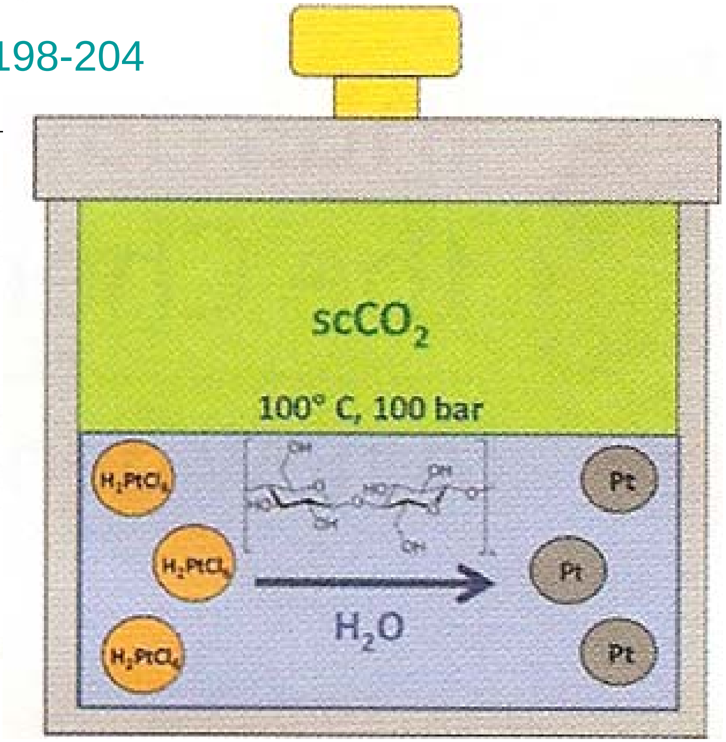
Making Nanomaterials in Supercritical Fluids: A Review

Xiangrong Ye and C. M. Wai* *J. Chem. Educ.* **2003**, *80*, 198-204

Synthesis of platinum nanoparticles using cellulosic reducing agents

Karima Benaissi, Lee Johnson, Darren A. Walsh and Wim Thielemans* *Green Chem*. **2010**, *12*, 35-38

The synthesis of platinum nanoparticle/cellulose nanocomposites using nanocrystalline cellulose from cotton in a water/supercritical carbon dioxide biphasic solvent system is described.



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

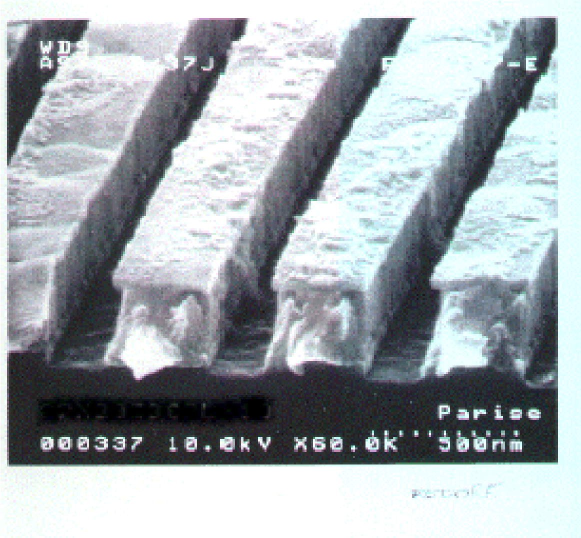
Alvin H. Romang and James J. Watkins*

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

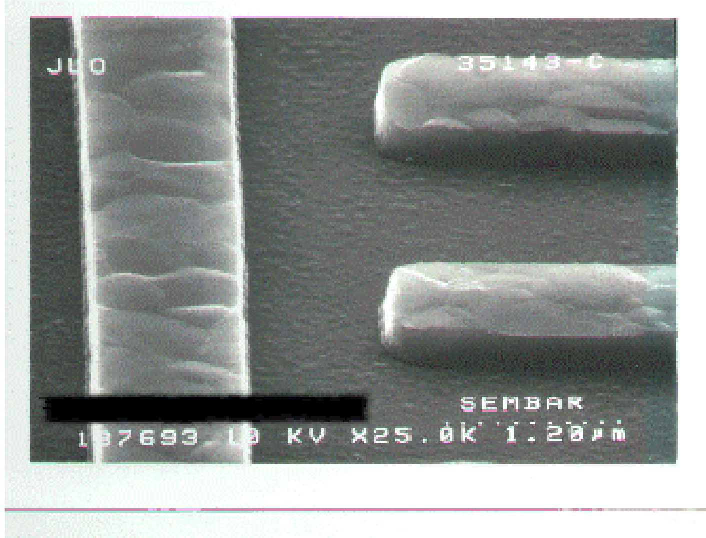
Chem. Rev. **2010**, *110*, 459-478

RIE Residue Removal

After metal etch

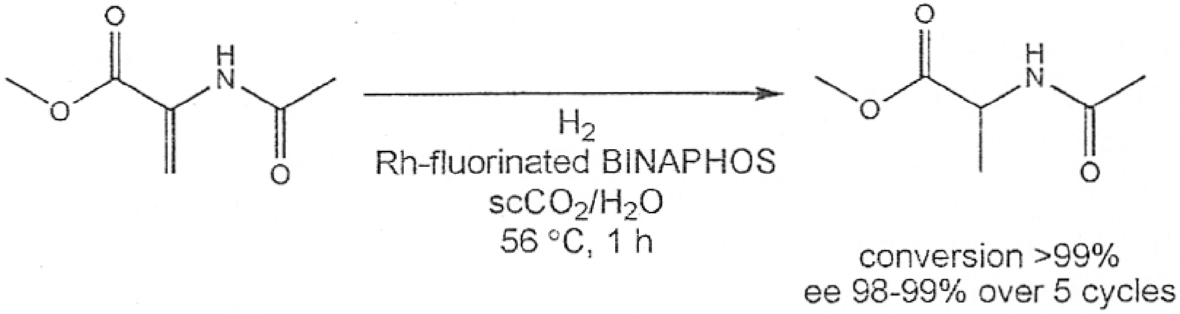


After SCCO2 cleaning



Examples

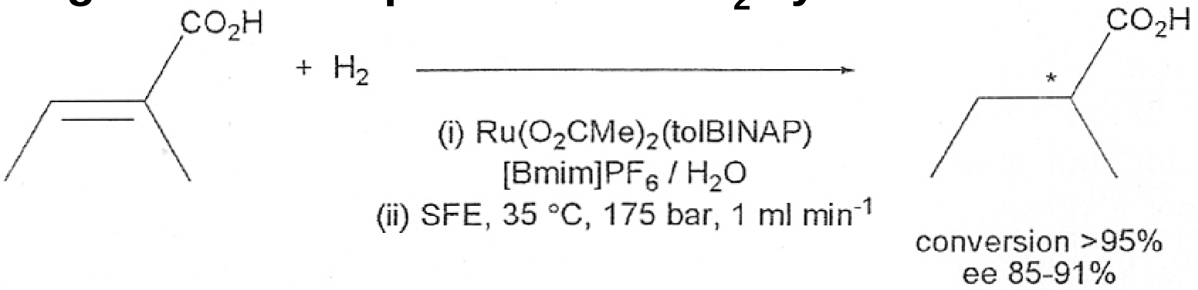
Enantioselective hydrogenation in $scCO_2$-H_2O system



H_2
Rh-fluorinated BINAPHOS
$scCO_2/H_2O$
56 °C, 1 h

conversion >99%
ee 98-99% over 5 cycles

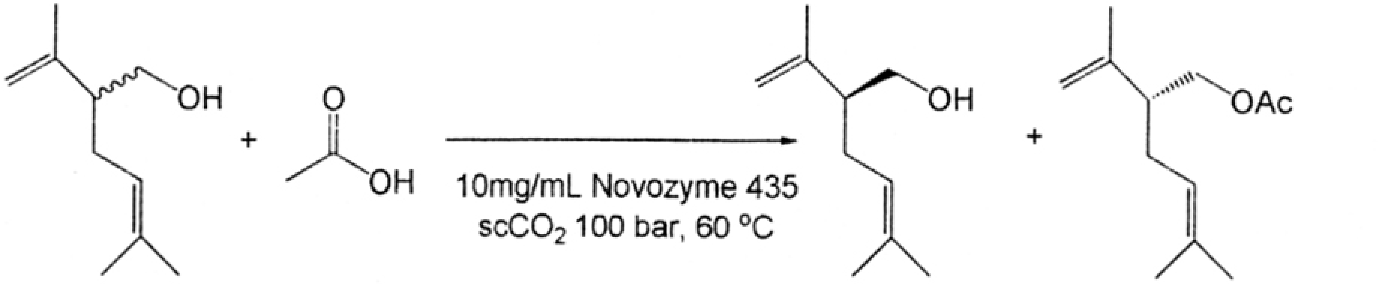
Hydrogenation in Biphasic IL-$scCO_2$ system



(i) $Ru(O_2CMe)_2$(tolBINAP)
$[Bmim]PF_6$ / H_2O
(ii) SFE, 35 °C, 175 bar, 1 ml min^{-1}

conversion >95%
ee 85-91%

Biocatalytic esterification



10mg/mL Novozyme 435
$scCO_2$ 100 bar, 60 °C

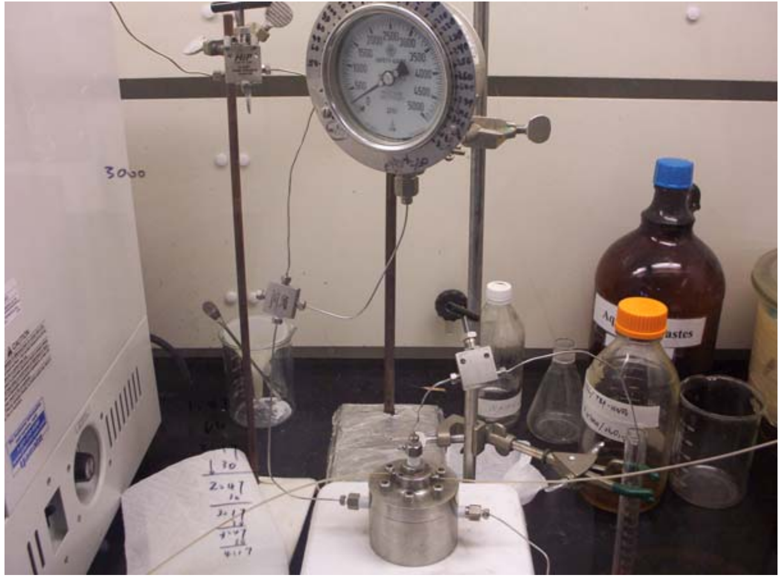
Racemic Lavandulol

(S)-Lavandulol

(R)- Lavandulyl acetate

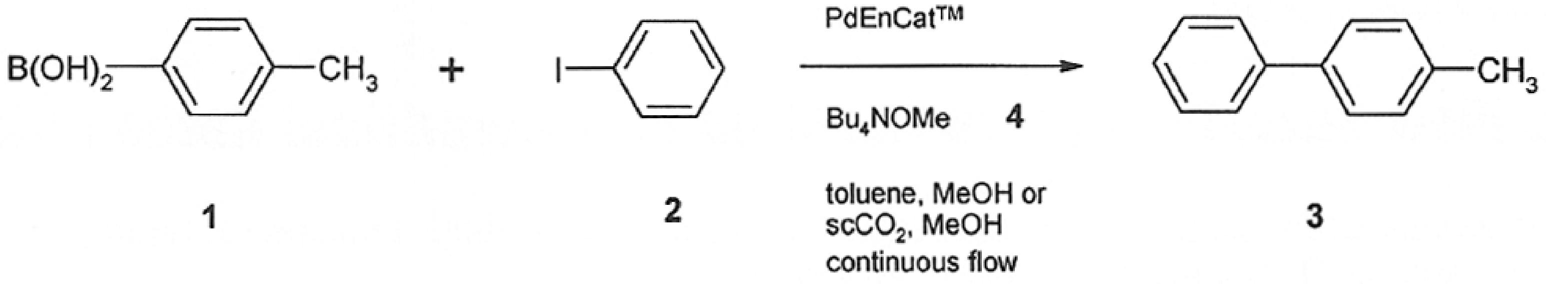
86%

(Kerton, pp. 81-82)

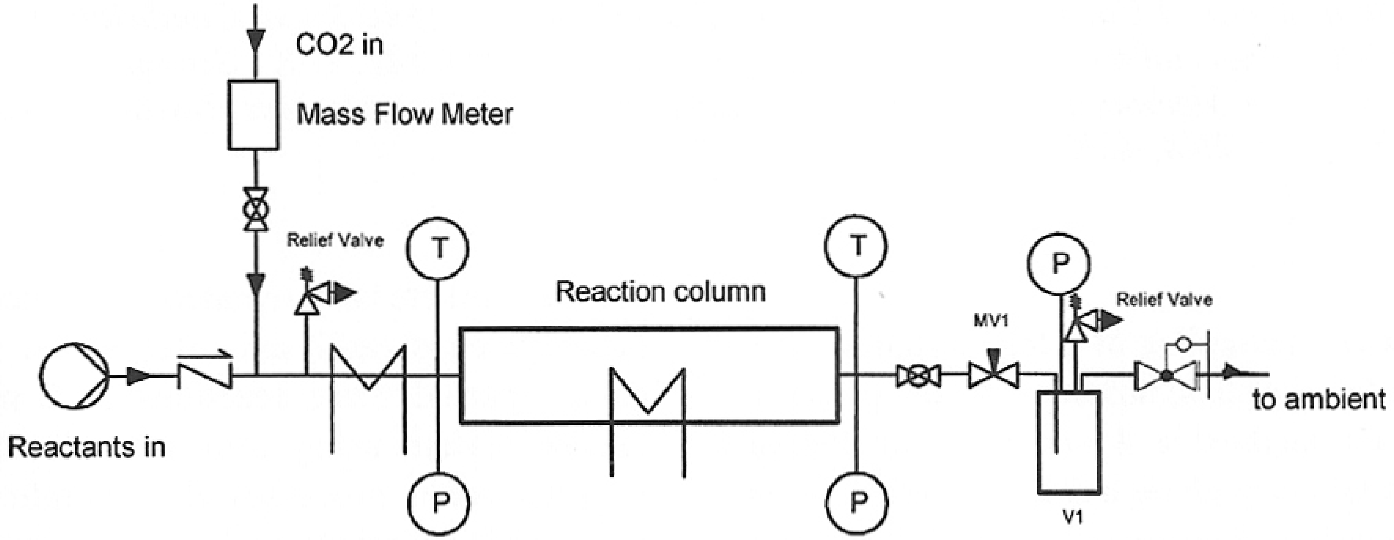


Courtesy of Professor C. M. Wai, U. Idaho.

Continuous-Flow Suzuki-Miyaura Reaction in SCF-CO_2



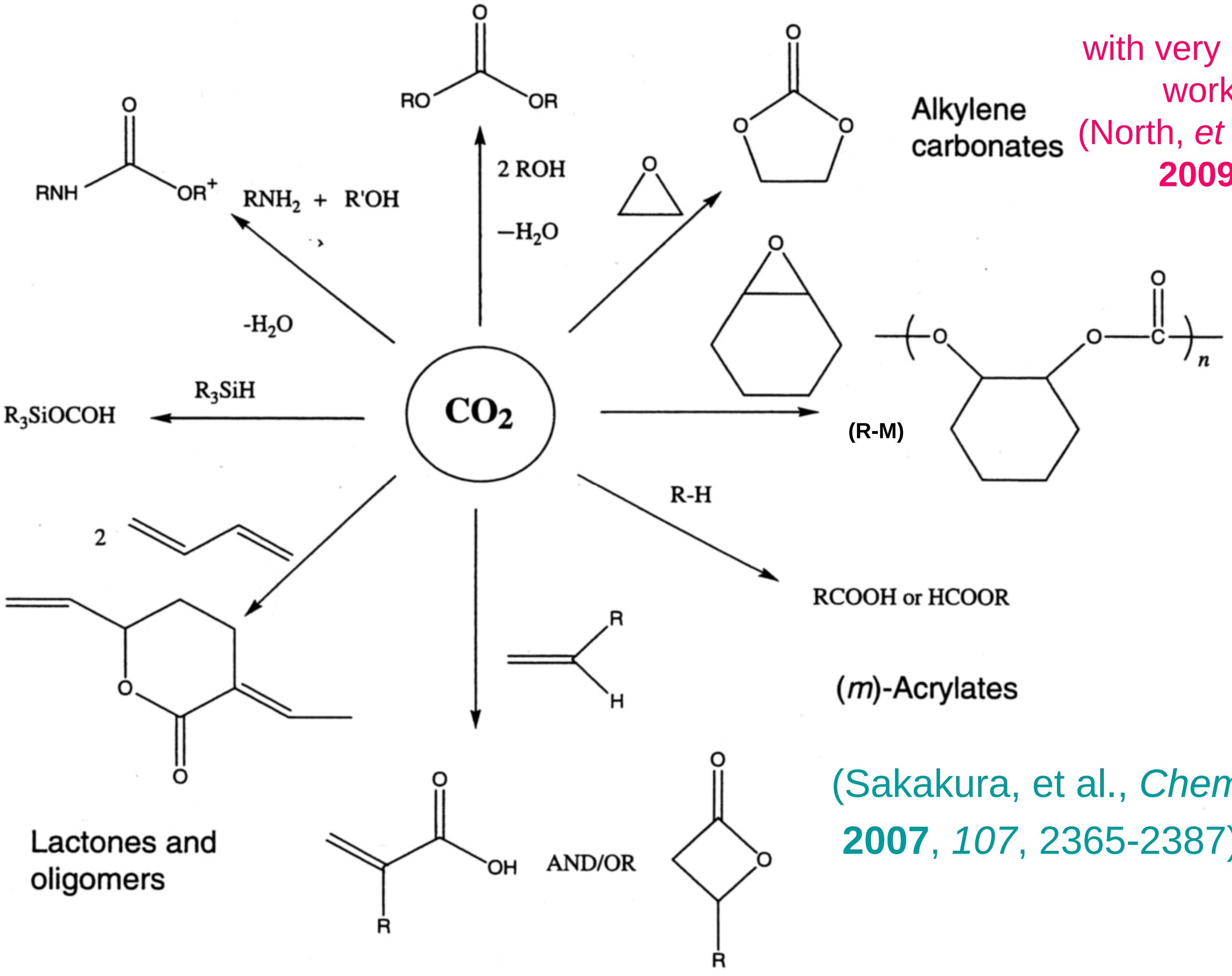
Suzuki−Miyaura preparation of 4-phenyltoluene 3 under continuous-flow conditions.



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

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

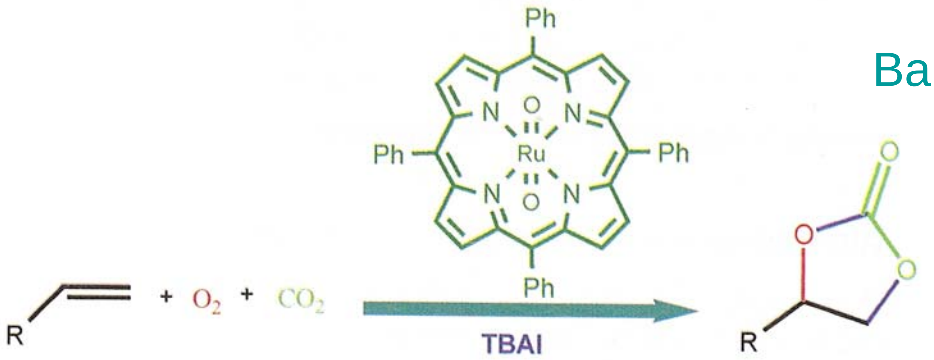
CO_2 Transformations



with very efficient catalyst working at 60°C (North, *et al. Chem. Eur. J.* **2009**, *15*, 11454)

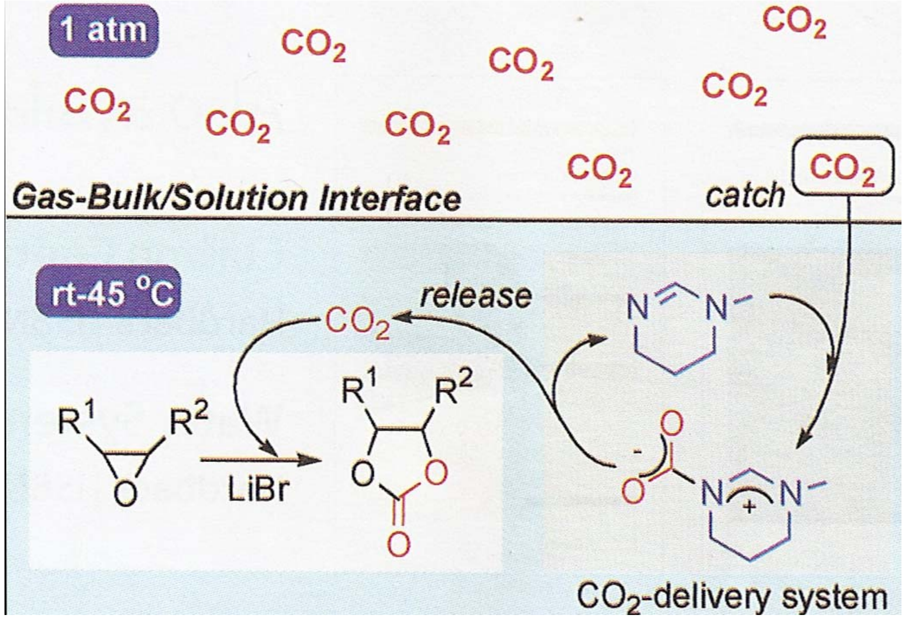
(Sakakura, et al., *Chem. Rev.* **2007**, *107*, 2365-2387)

Aerobic oxidative carboxylation of olefins with metalloporphyrin catalysts



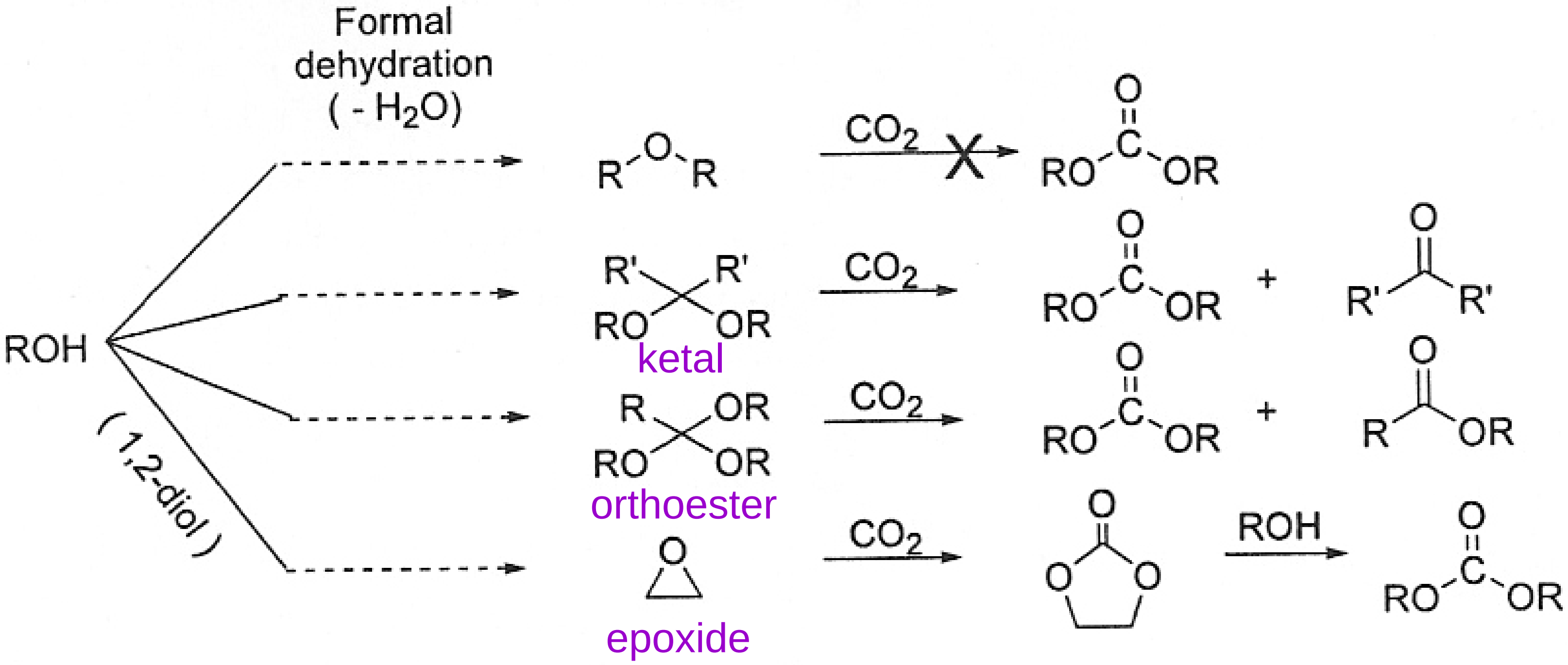
Bai and Jing, *Green Chem*. **2010,** *12,* 39-41

Amidine-mediated delivery of CO_2 from gas phase to reaction system for highly efficient synthesis of cyclic carbonates from epoxides



Barkakaty, et al., *Green Chem*. **2010,** *12,* 42-44

Dialkyl carbonate from CO_2



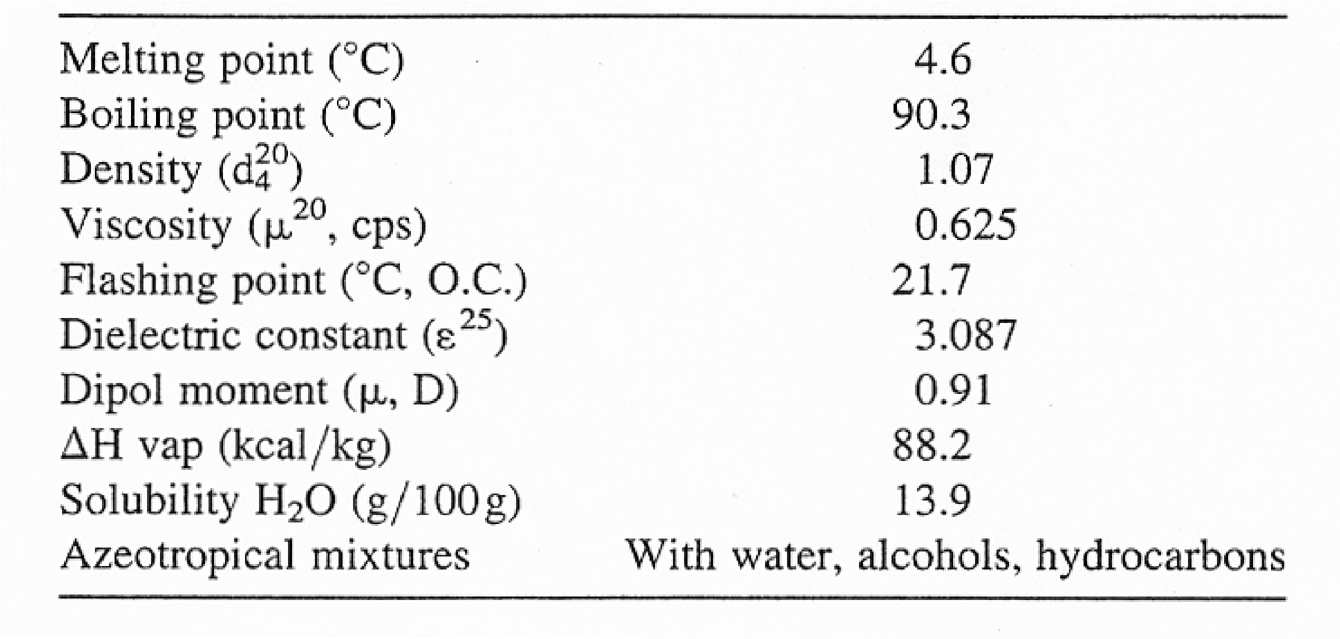
Production of dimethyl carbonate from ethylene oxide and CO_2 as a more effective way for the reuse of CO_2

(*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

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

$\geqq$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)

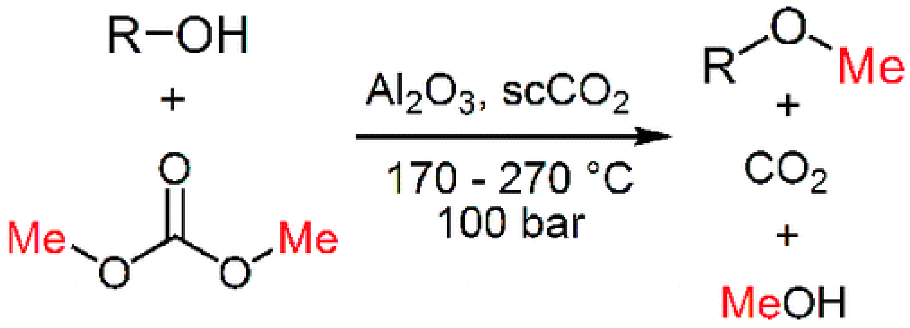
Green chemistry metrics: a comparative evaluation of dimethyl carbonate, methyl iodide, dimethyl sulfate and methanol as methylating agents

(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.

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

Continuous Acid-Catalyzed Methylations in Supercritical CO_2: Comparison of Methanol, Dimethyl Ether and Dimethyl Carbonate as Methylating Agents

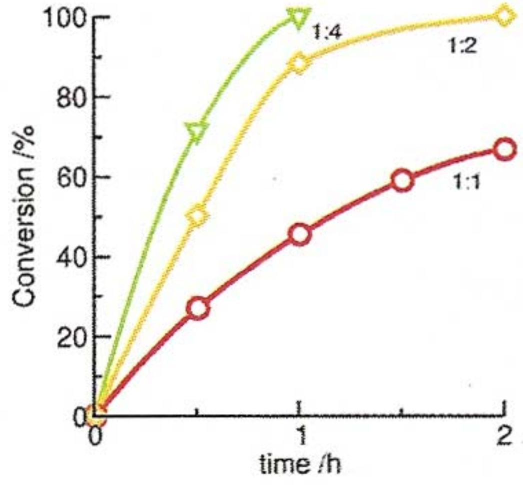


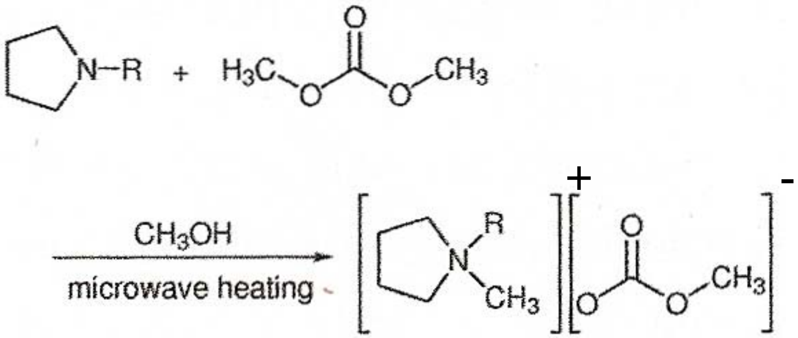
Org. Proc. Res. Dev. **2010**, *14*, 411-416

(Poliakoff and coworkers)

Optimised MW-assisted synthesis of methylcarbonate salts: a convenient methodology to prepare intermediates for ionic liquids

Holbrey, et al., *Green Chem***.** **2010,** *12*, 407-410





100% yield at 130℃ for 1 hr, R = Bu

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)

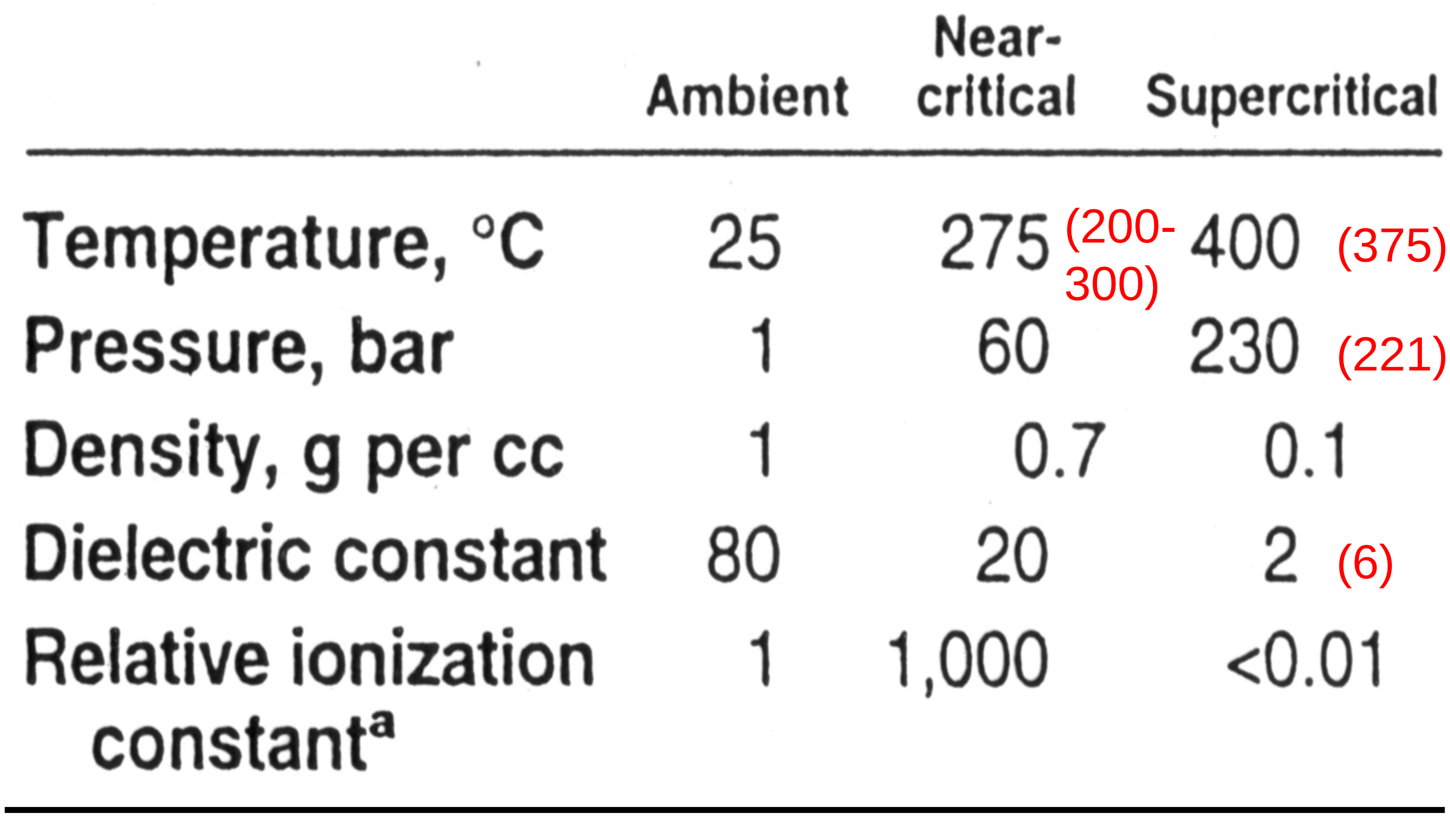
Table 5.4 *Advantages and disadvantages of using water as a solvent*

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	

Lancaster, *Green Chemistry*, p. 149

Odorless and looked colorless (most contaminations are easy to recognize)	Some compounds or catalysts react with water in an adverse way. Water-soluble catalyst is difficult to recover. Recovery and reuse

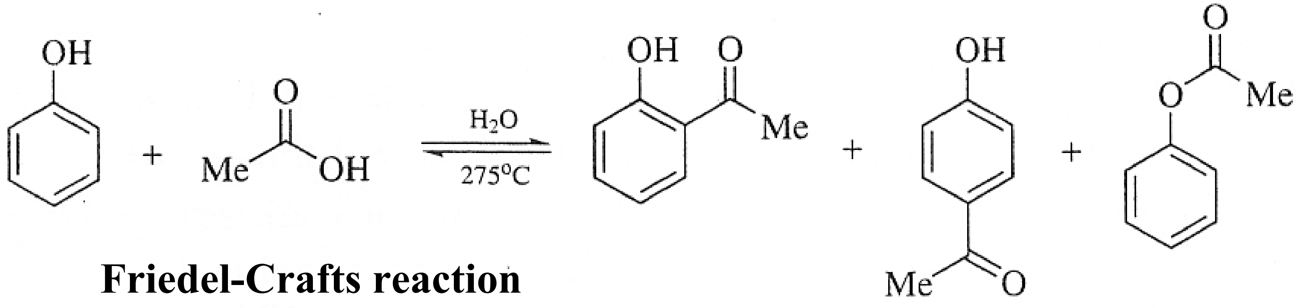
Dielectric and ionization constants



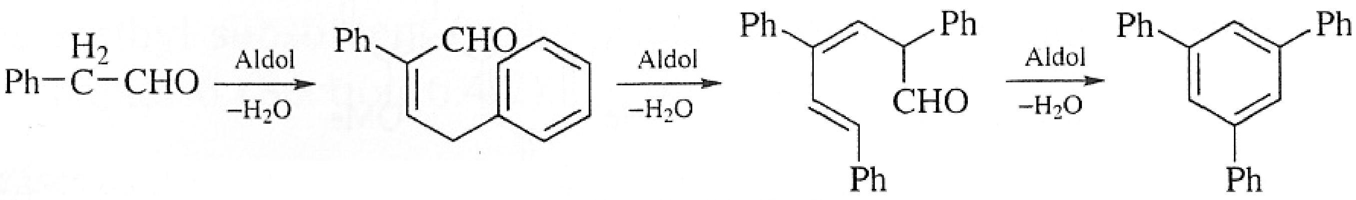
	Ambient	Near-critical	Supercritical
Temperature, °C	25	275 (200-300)	400 (375)
Pressure, bar	1	60	230 (221)
Density, g per cc	1	0.7	0.1
Dielectric constant	80	20	2 (6)
Relative ionization constant[a]	1	1,000	<0.01

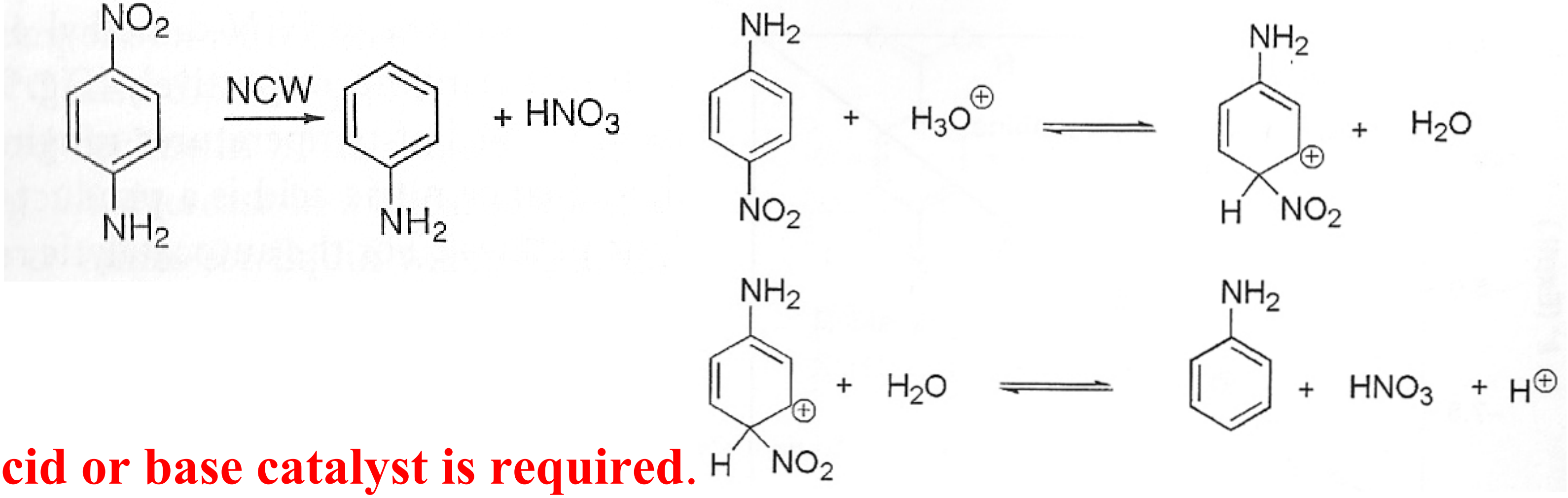
[a] **K_W/K_W(25℃)**

Reactions in near-critical water (NCW)



Friedel-Crafts reaction



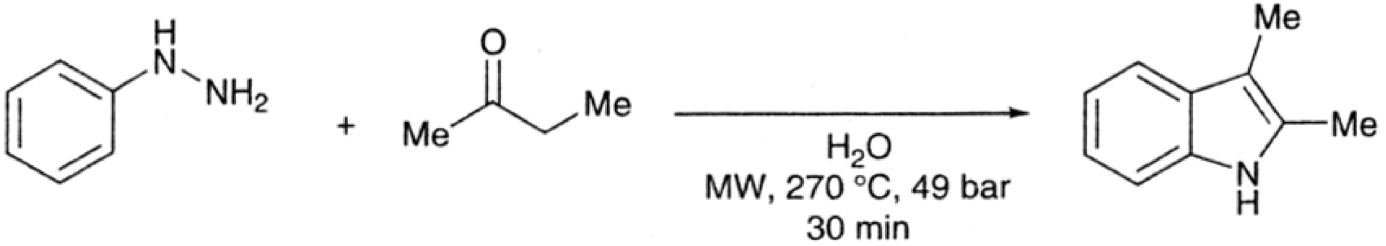


No acid or base catalyst is required.

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

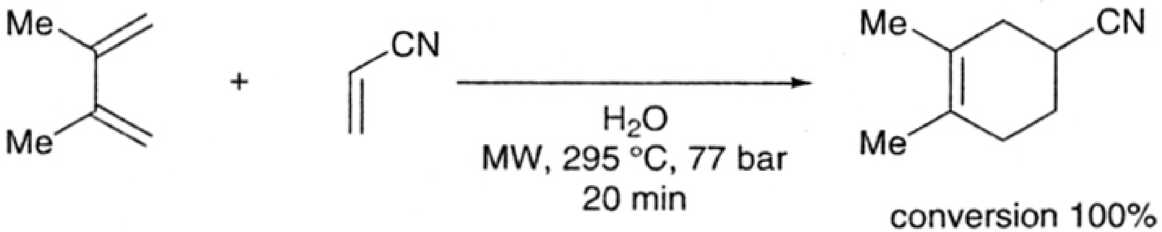
Some microwave assisted reactions at NCW

Fischer indole synthesis



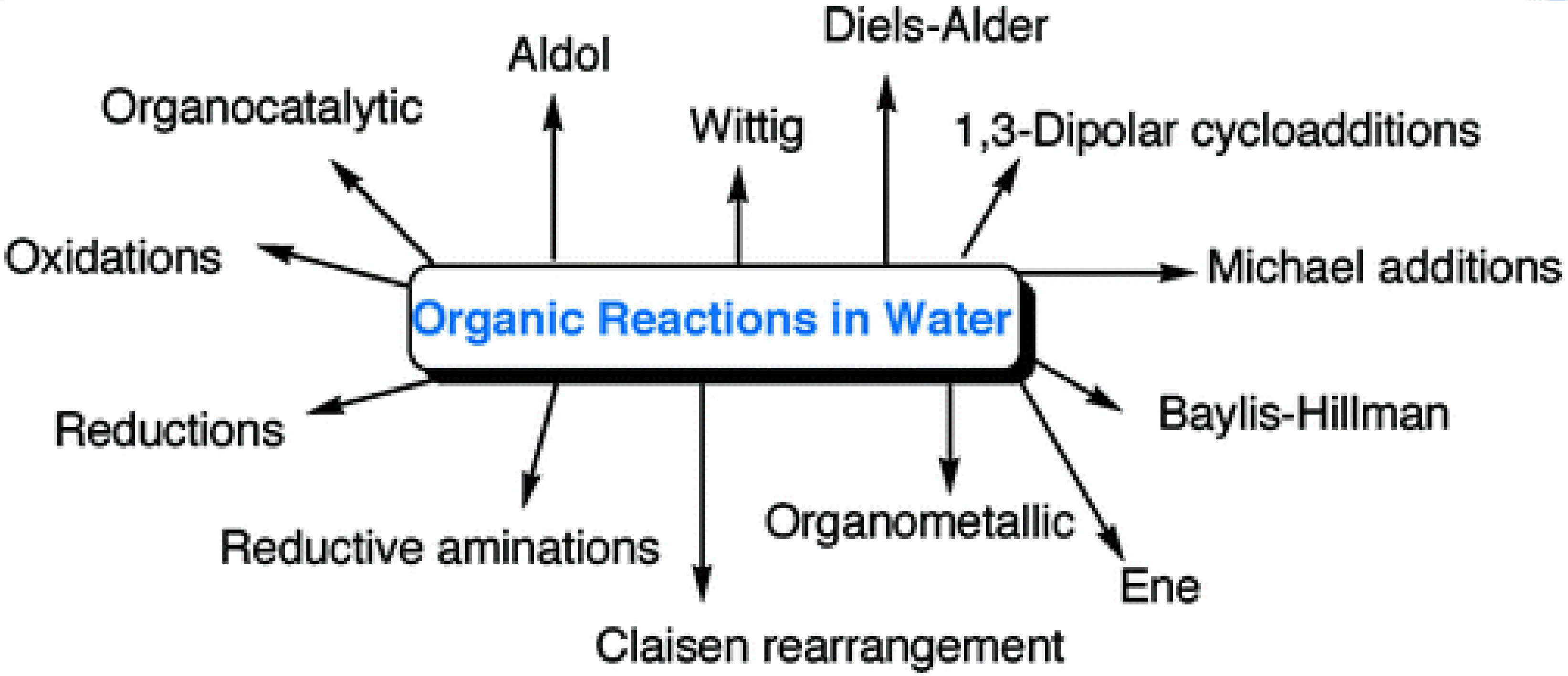
isolated yield 64%
(column chromatography, CH_2Cl_2)

Diels-Alder reaction



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

(Kerton, p. 88)



Organic Reactions in Water

Aldol

Diels-Alder

Organocatalytic

Wittig

1,3-Dipolar cycloadditions

Oxidations

Michael additions

Reductions

Baylis-Hillman

Reductive aminations

Organometallic

Ene

Claisen rearrangement

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

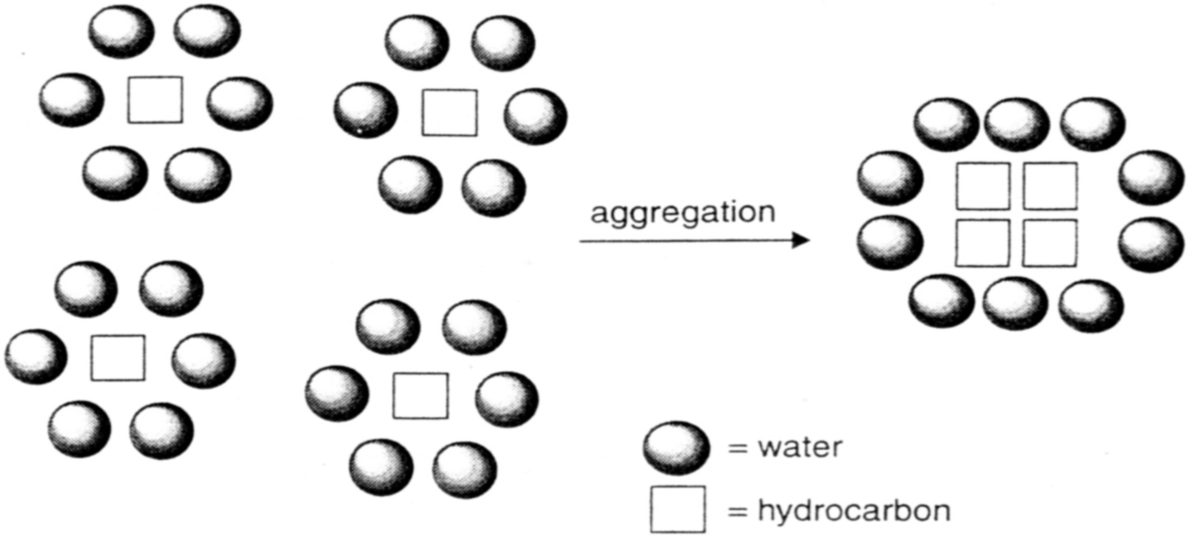
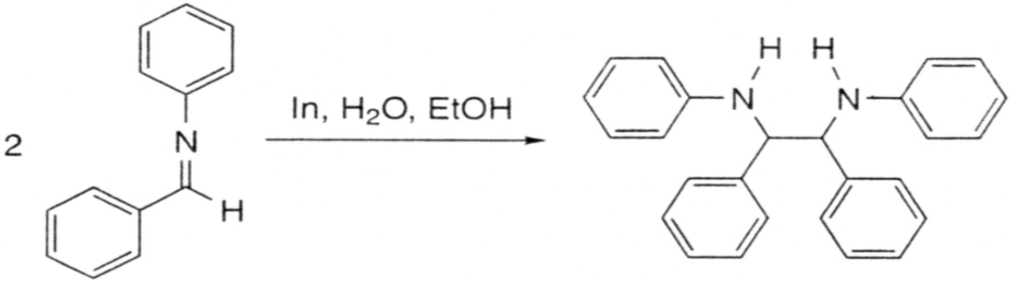


Figure 5.5 The hydrophobic effect. Aggregation of hydrocarbon molecules in water reduces the number of molecules with restricted motion

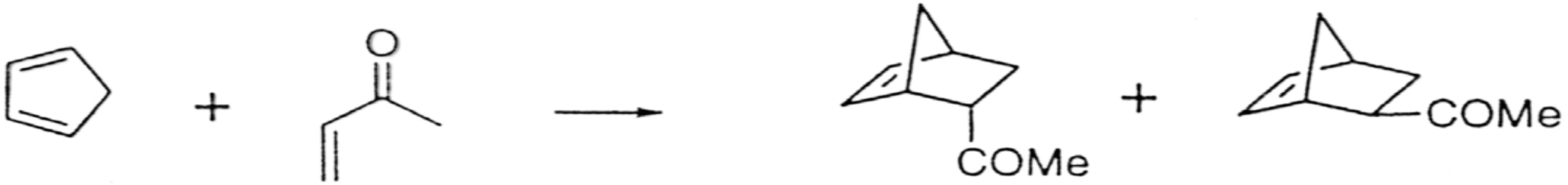


Scheme 5.1 Indium mediated imine coupling

(Adams, p.101)

Diels-Alder Reaction

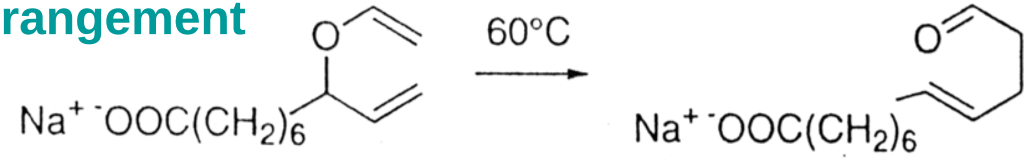
Enhanced Selectivity and Reactivity



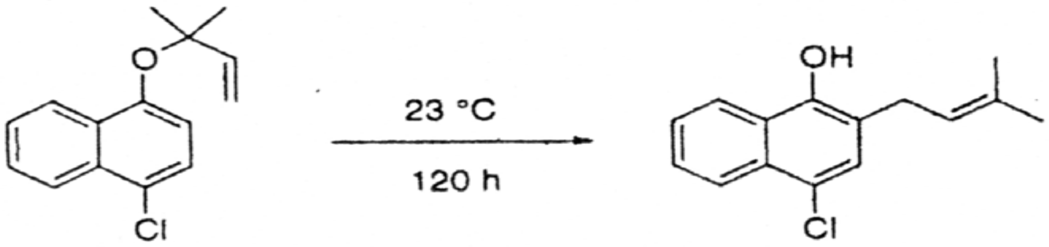
solvent	kinetics 10^5 k ($M^{-1}s^{-1}$)	selectivity endo/exo ratio
isooctane	5.94[a]	
methanol	75.5[a]	8.5[c]
formamide	318[b]	8.9[b]
ethylene glycol	480[b]	10.4[b]
water	4400[a]	25[d]
water (LiCl 4.86 M)	10800[a]	28[d]
water ($(NH_2)_3CCl$ 4.86 M)	4300[a]	22[d]
β-cyclodextrin (10 mM)	10900[a]	
α-cyclodextrin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



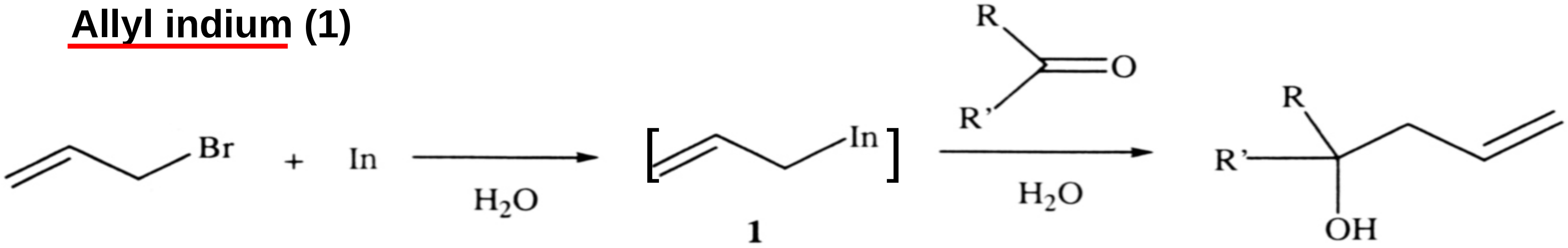
12

13
(m.p.: 54–56 °C)

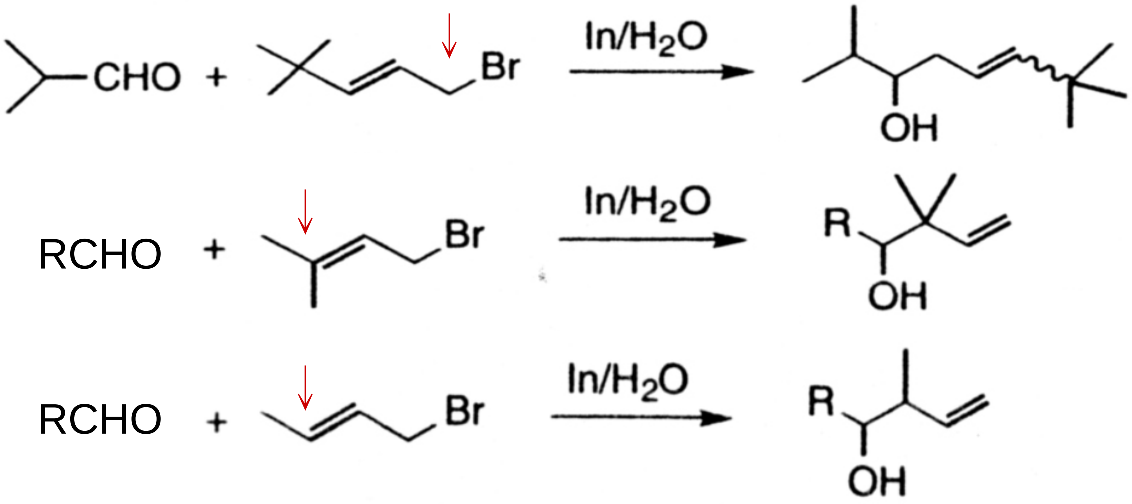
Solvent	Yield [%][b]
toluene	16
DMF	21
CH_3CN	27
MeOH	56[c]
neat	73
on H_2O	**100**

Grignard-type Reactions

Allyl indium (1)

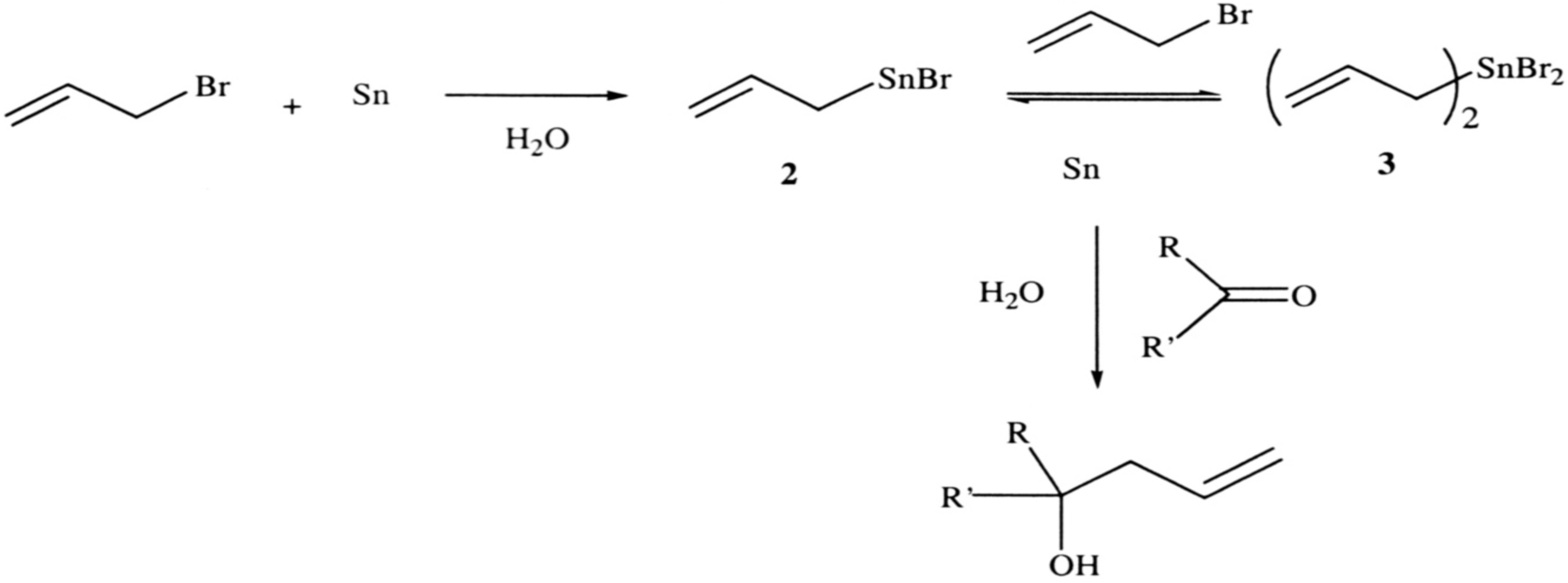


Indium has low first ionization potential (5.70 eV), and is not sensitive to water or base. The regioselectivity is governed by the bulkiness of the substituent on the C=C.

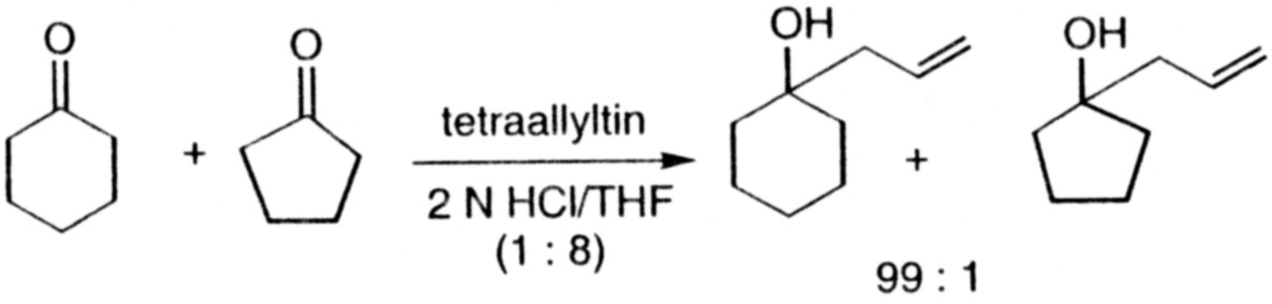


Grignard-type Reactions

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).

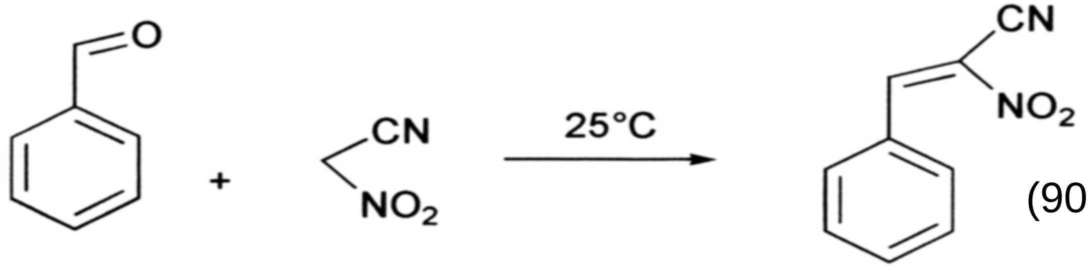


High chemoselectivity



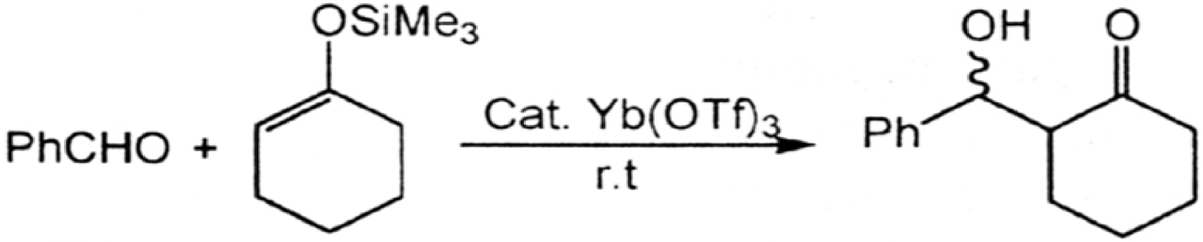
Other C-C bond formations

Condensation of active methylene compounds



(90% yield)

Mukaiyama aldol reactions

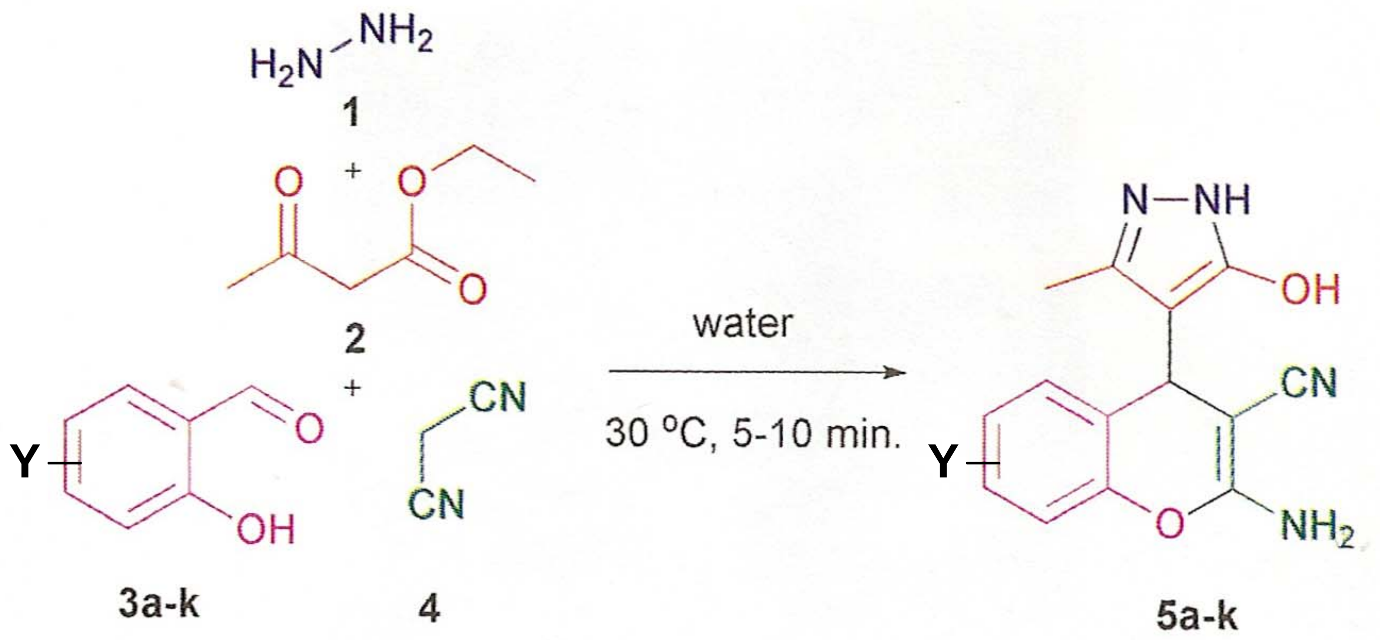


34 35 36

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

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

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

Controlled/'living" radical polymerization applied to water-borne systems Matyjaszewski, *Macromol. 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.

2009 PGCC Academic Award to Professor Matyiaszewski of Carnegie Mellon U. **Atom Transfer Radical Polymerization: Low-impact Polymerization Using a Cu Catalyst and Environmentally Friendly Reducing Agents.** 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.

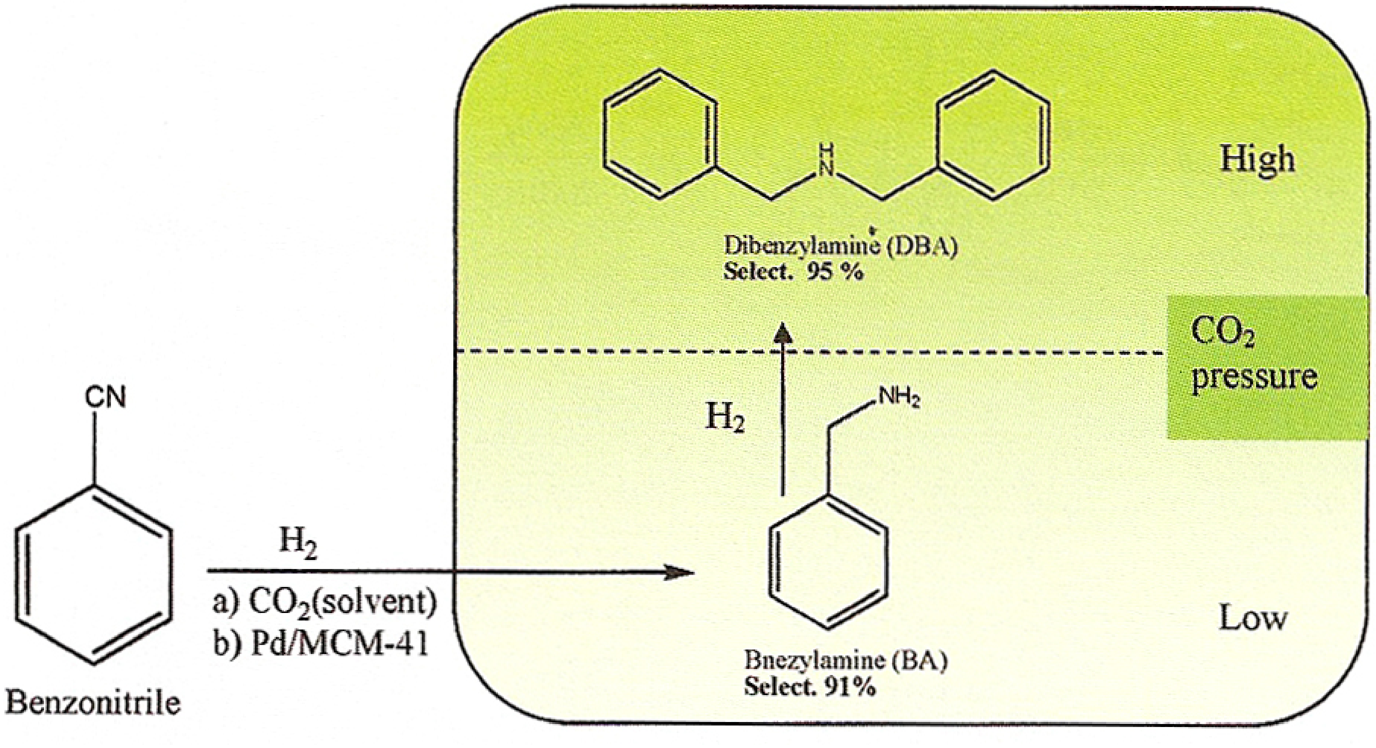
Hydrogen atom transfer (HAT) reactions in aqueous media. A mechanistic study

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

Hydrogenation of nitrile in $scCO_2$: a tunable approach to amine selectivity

Chatterjee, *et al. Green Chem*. **2010**, *12*, 87-93

By tuning the CO_2 pressure changes the product selectivity (more than 90%) from benzylamine to dibenzylamine, with 90+% conversion.



Organic Reactions on Silica in Water

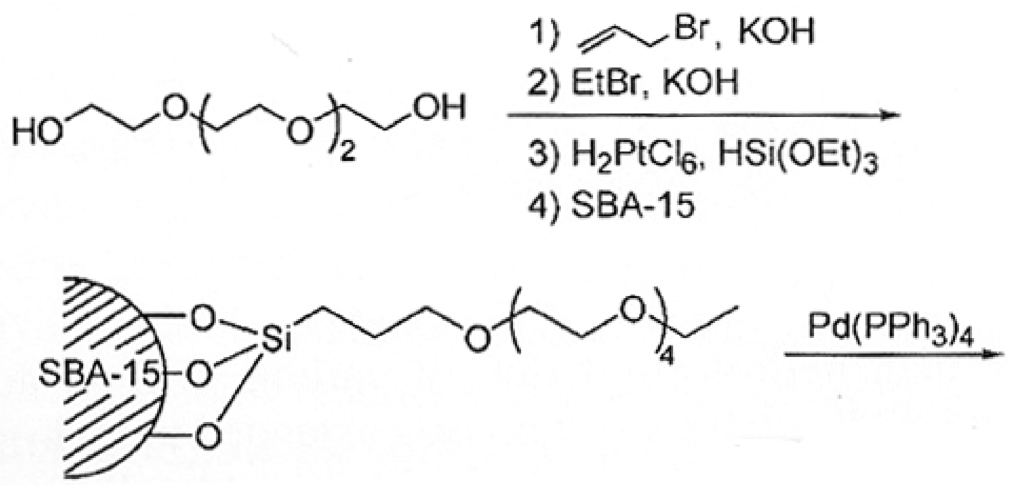
Minakata and Komatsu, *Chem. Rev*. **2009**, *109*, 711-724

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

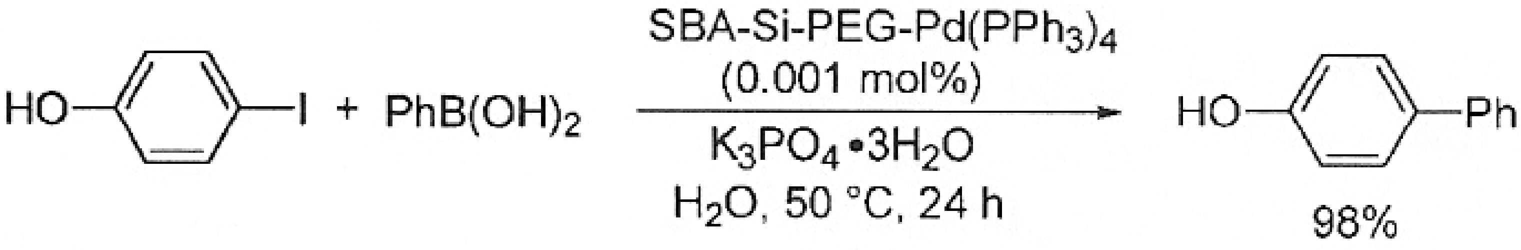
1. Immobilization of catalysts on silica supports in a water-only phase.
2. To employ a biphasic system:
    Water – organic solvent
    Water – ionic liquid
    Fluorous reverse-phase silica and water

Silica without modification is also generally used.

Mesoporous Silica-supported catalyst and Suzuki Coupling

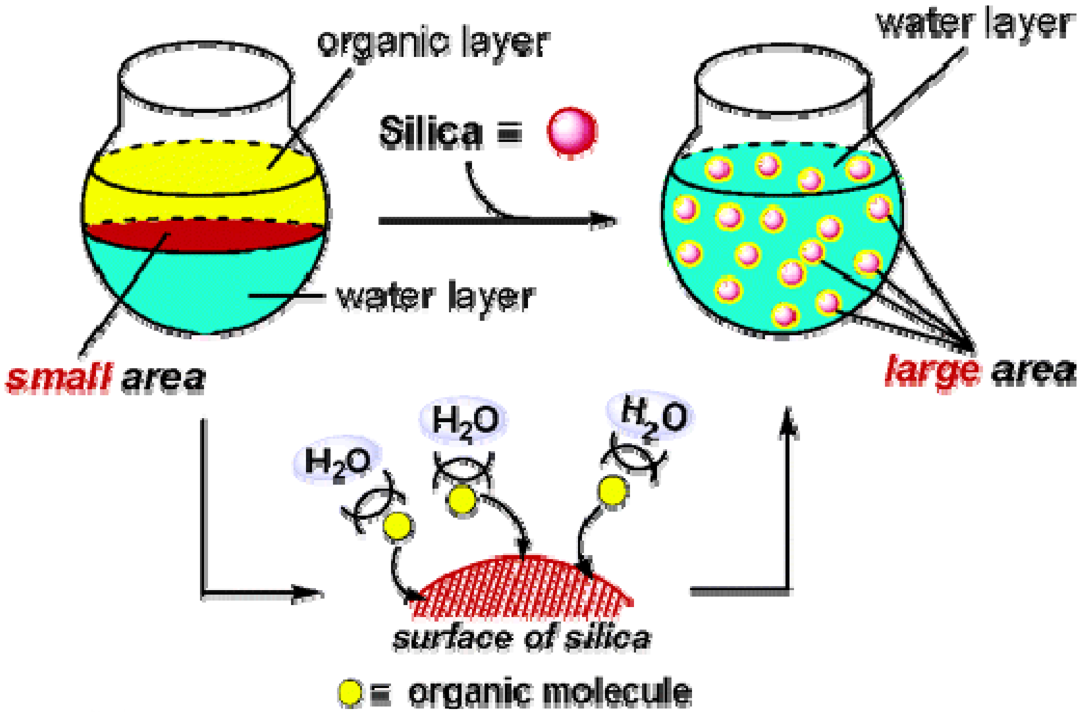


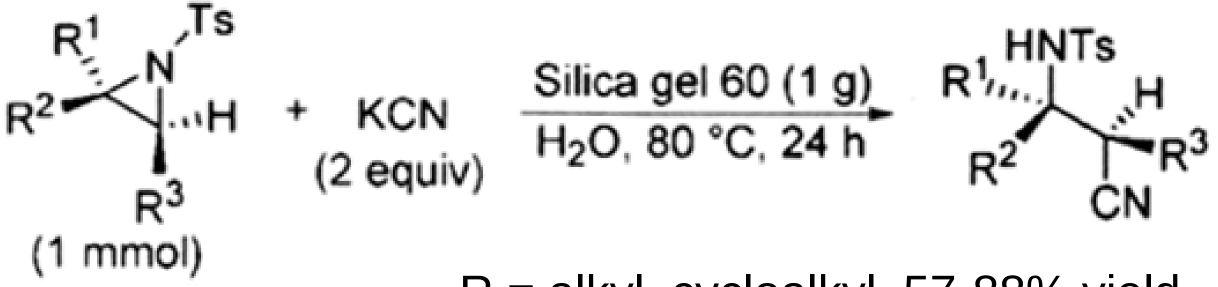
SBA-Si-PEG-$Pd(PPh_3)_4$



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

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



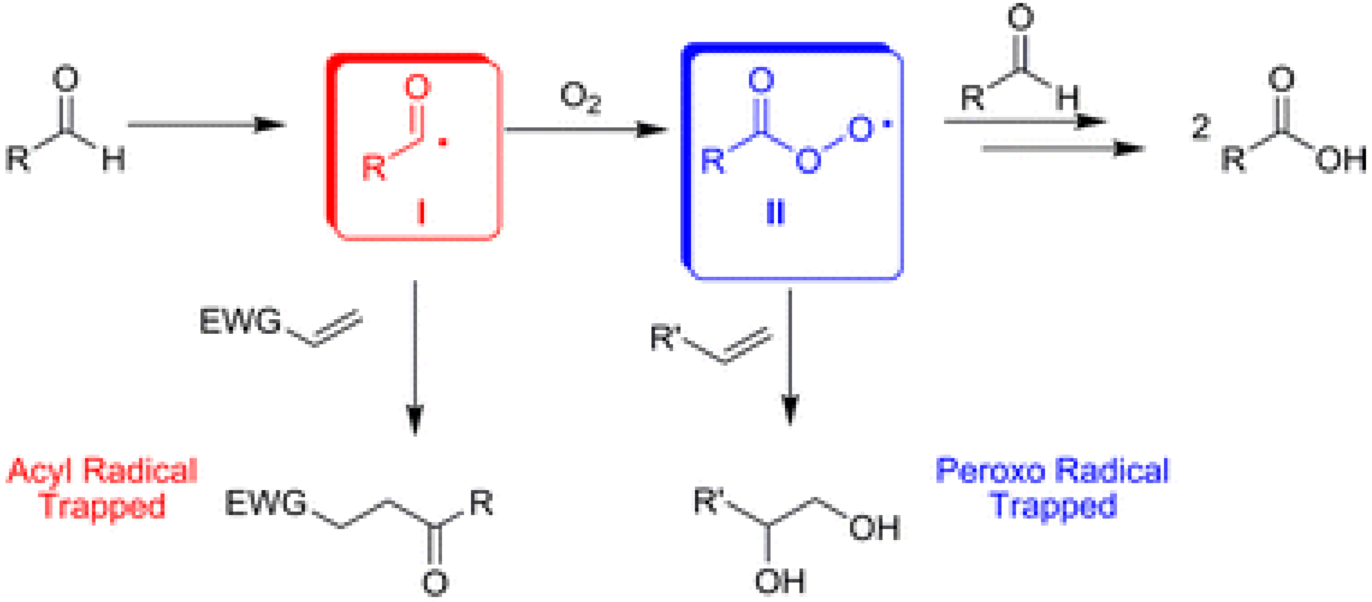


R = alkyl, cycloalkyl, 57-88% yield

Straightforward radical organic chemistry in neat conditions and on water

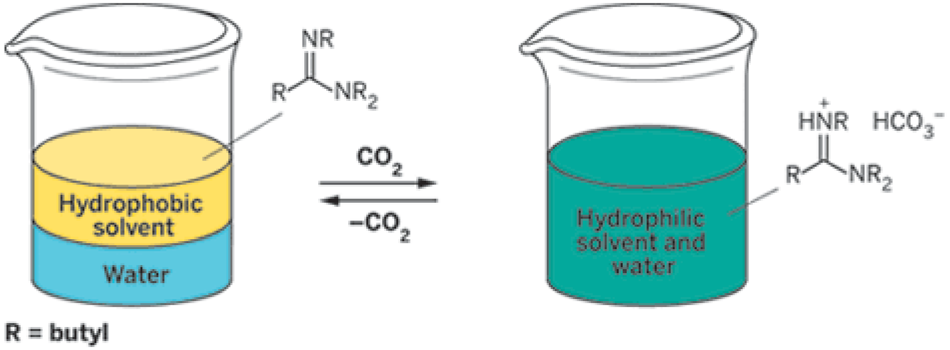
Shapiro et al., *Green Chem.*, **2010**, *12*, 582 - 584

Radicals generated during aldehyde oxidation to carboxylic acids can be efficiently trapped under environmentally friendly conditions, either in neat conditions or "on water."

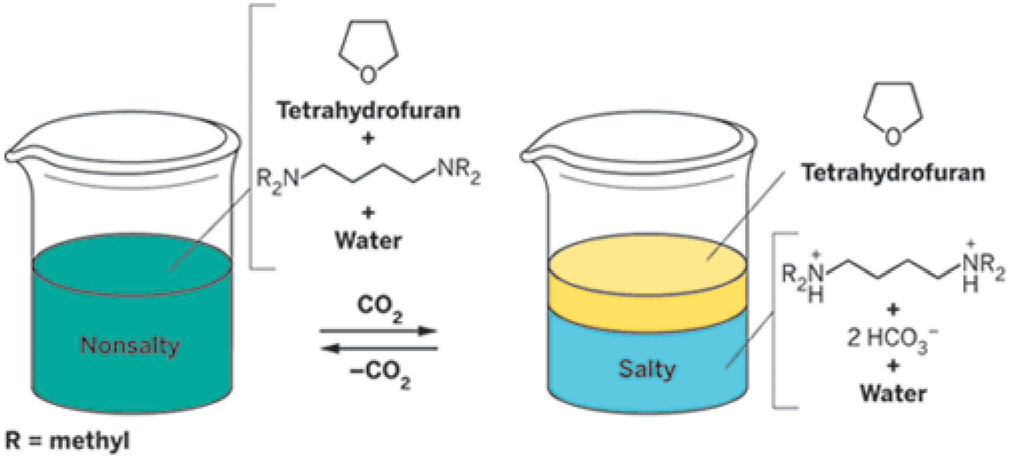


Switchable Water: Aqueous Solutions of Switchable Ionic Strength

Mercer and Jessop, *ChemSusChem* **2010**, *3*, 467-470



Switchable hydrophilicity solvent

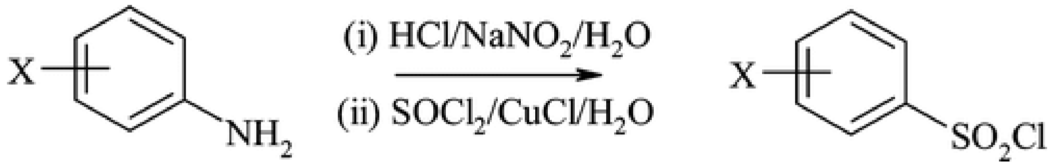


Switchable water

Aqueous Process Chemistry

The Preparation of Aryl Sulfonyl Chlorides

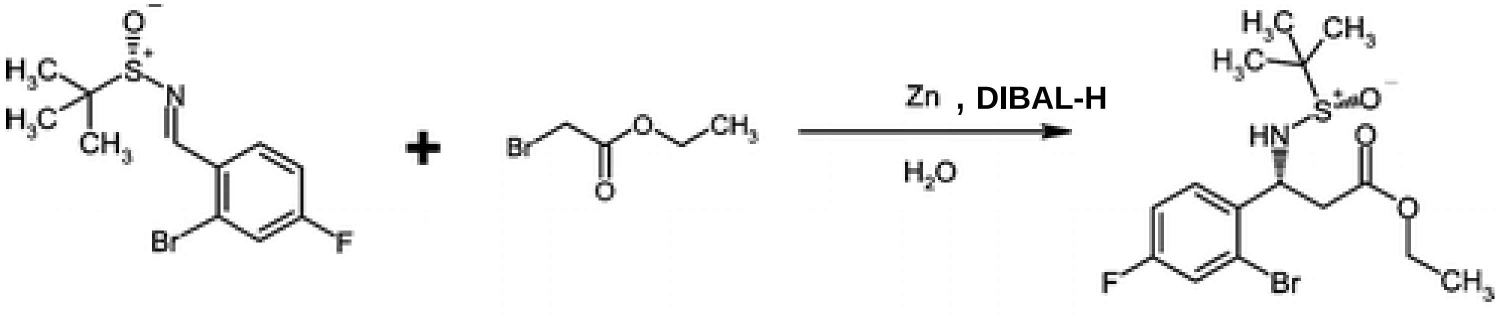
Hogan and Cox**,** *Org. Proc. Res. Dev.*, **2009**, *13*, 875–879



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

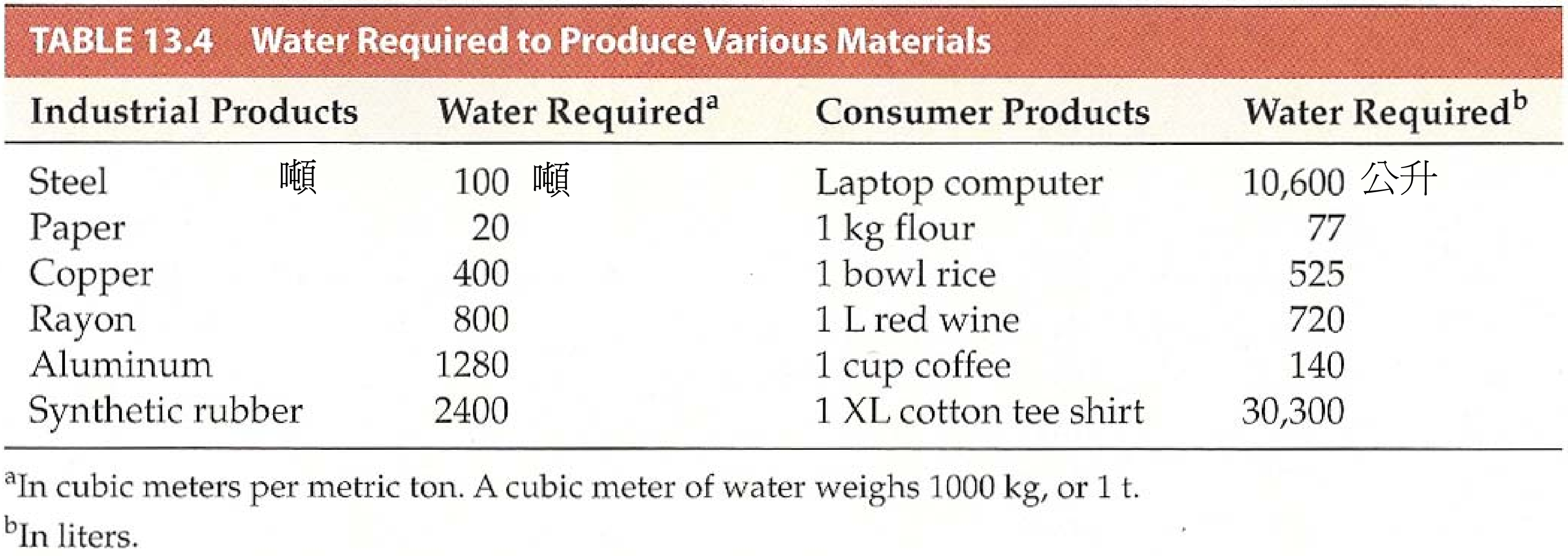


TABLE 13.4 Water Required to Produce Various Materials

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:

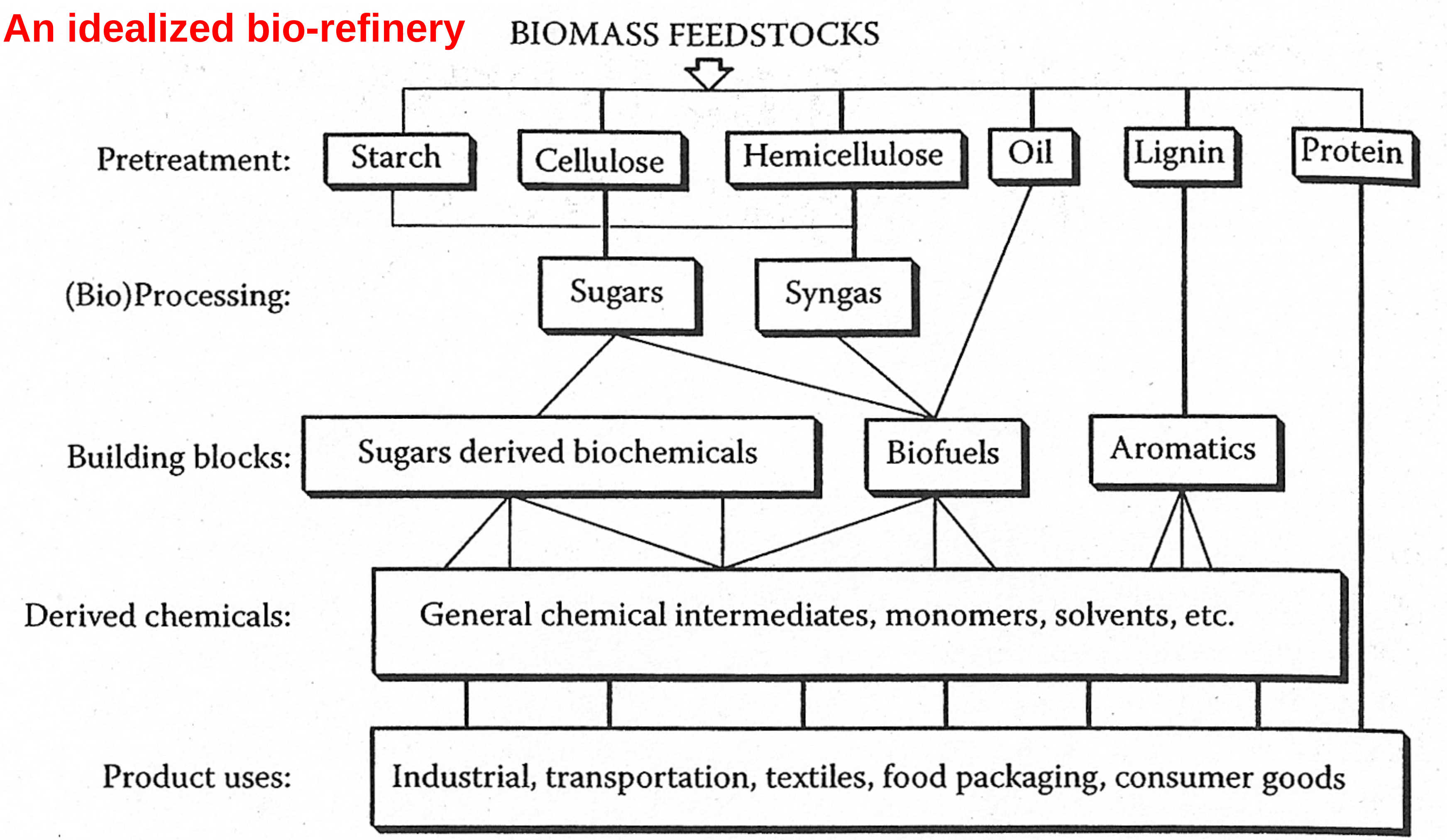
- Corma, *et al. Chem. Rev.* **2007**, *107*, 2411-2502 (general)
- Meier, *et al. Chem. Soc. Rev.* **2007**, *36*, 1788-1802 (polymers)
- Behr, *et al. Green Chem.* **2008**, *10*, 13-30 (glycerol)
- Delhomme, *et al. Green Chem.* **2009**, *11*, 13-26 (succinic acid)
- Bozell and Peterson, *Green Chem.* **2010**, *12*, 539-554 (biorefinery carbohydrates)

and many more

Renewable resources:

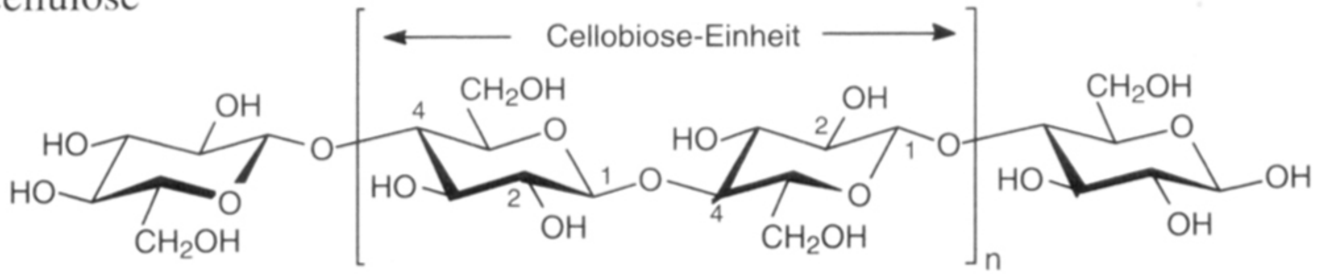
Carbohydrates (sugar, starch, cellulose, etc.), 75%
Lignin, 20%
Fats and oils, proteins, terpenes, etc., 5%

An idealized bio-refinery



Carbohydrates

Cellulose



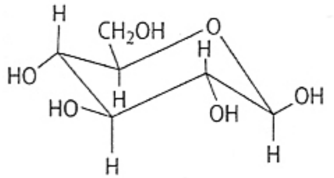
starch

α -1,4'-glycosidic linkage

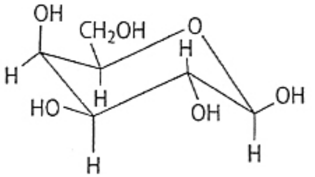
β -1,4'-glycosidic linkage

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

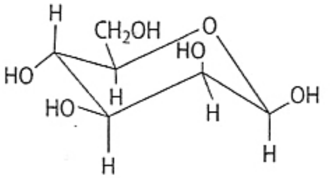
Sucrose (glucose and fructose)



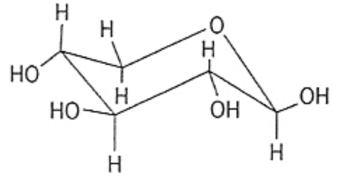
Glucose



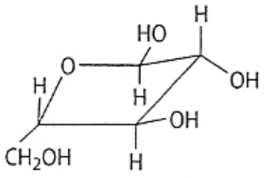
Galactose



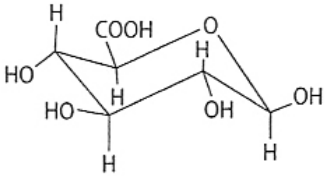
Mannose



Xylose



Arabinose

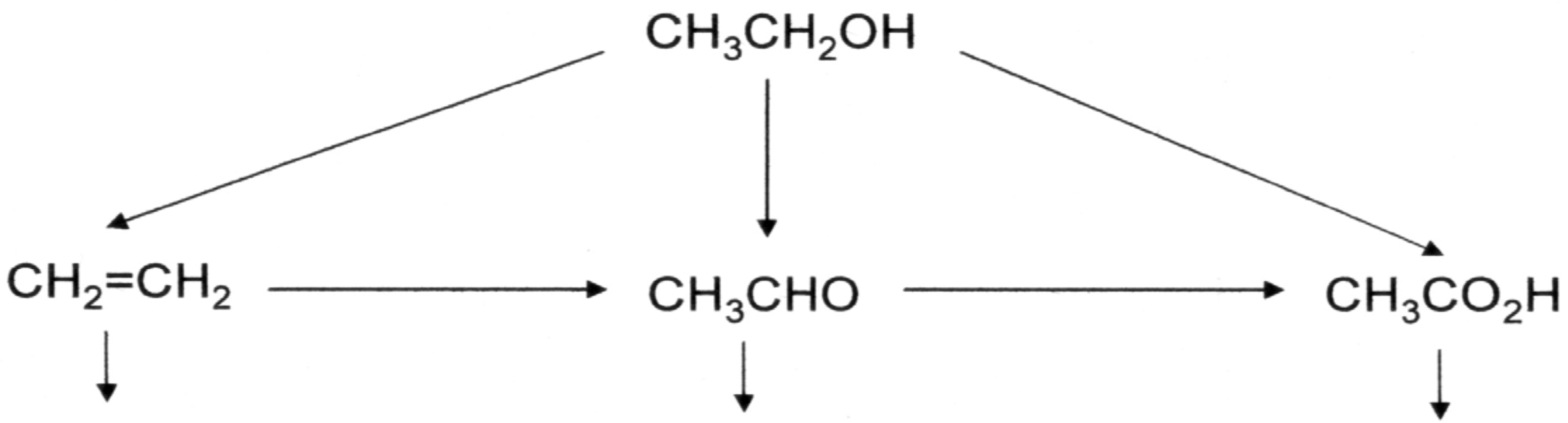


Glucuronic acid

醣類發酵產生乙醇： **e.g.** $C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH$(ethanol) + $2CO_2$

Sorbitol, Xylitol $C_5H_{12}O_5$, $HOCH_2(CHOH)_3CH_2OH$ isomers

Chemicals from ethanol



CH_3CH_2OH

$CH_2{=}CH_2$ → CH_3CHO → CH_3CO_2H

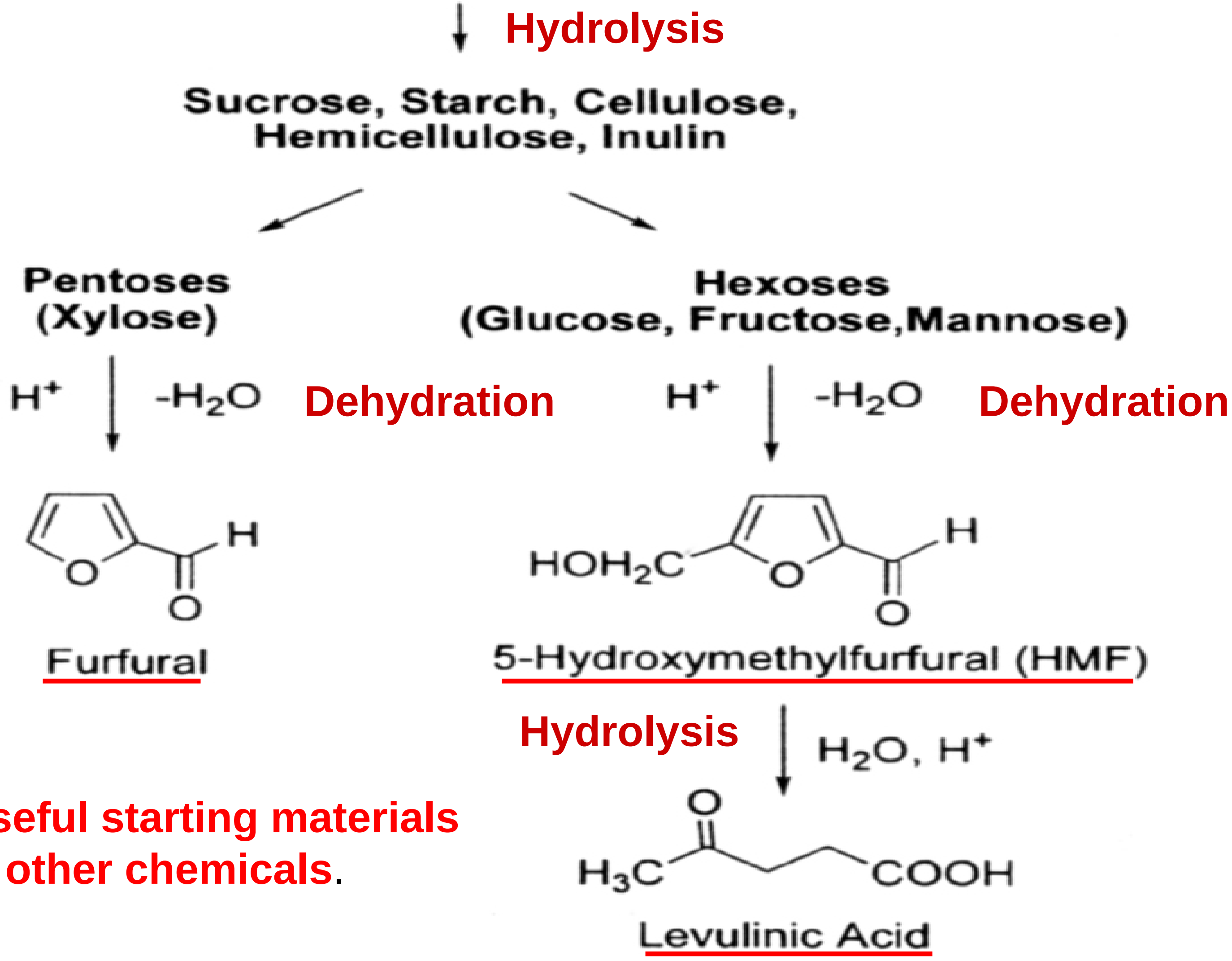
Ethyl benzene
Ethyl bromide
Ethyl chloride
Ethylene chlorohydrin
Ethylene diamine
Ethylene dibromide
Ethylene dichloride
Ethylene glycol
Ethyleneimine
Ethylene oxide
Diethyl ketone
Diethylene glycol
Glycol ethers, esters
MEA, DEA, TEA
Vinyl acetate
Polymers, copolymers
....

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

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)



Hydrolysis

Sucrose, Starch, Cellulose,
Hemicellulose, Inulin

Pentoses
(Xylose)

Hexoses
(Glucose, Fructose,Mannose)

H^+ $-H_2O$ Dehydration

H^+ $-H_2O$ Dehydration

Furfural

5-Hydroxymethylfurfural (HMF)

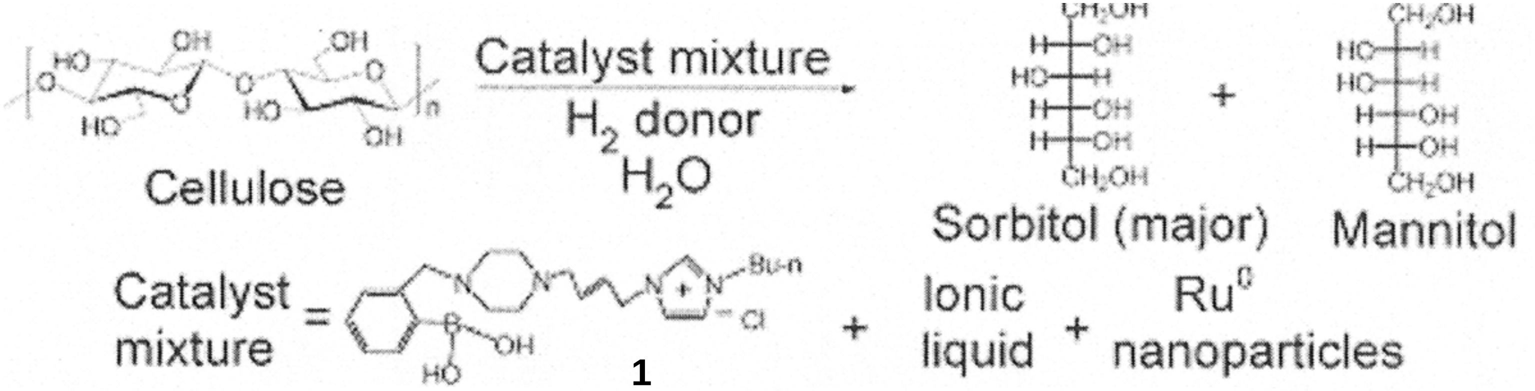
Hydrolysis H_2O, H^+

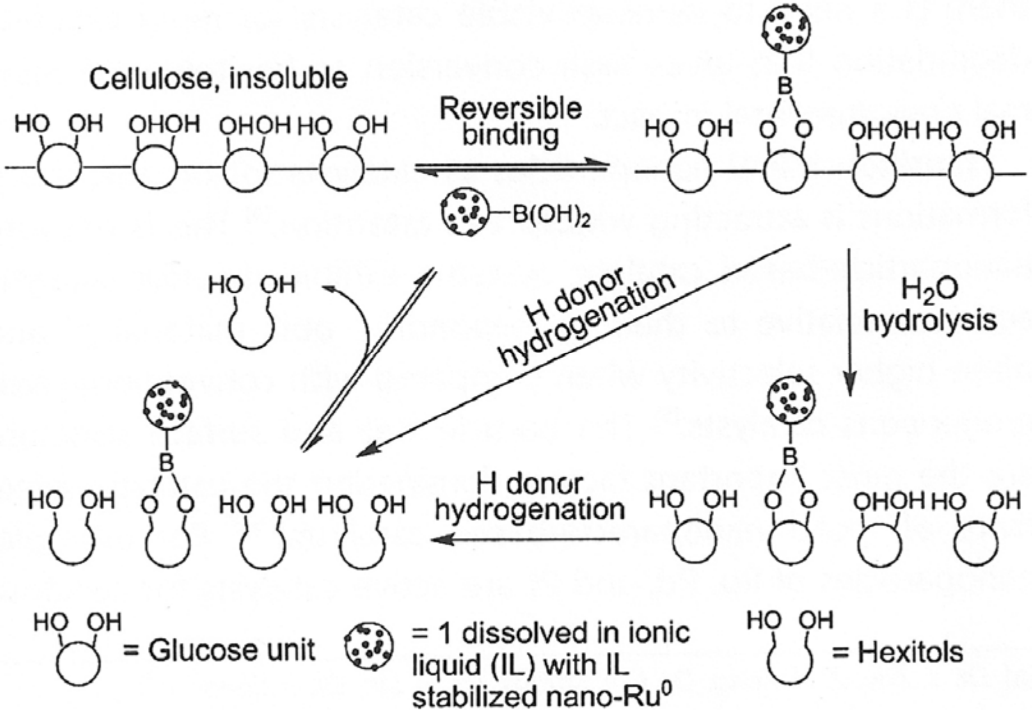
Levulinic Acid

They are useful starting materials
for making other chemicals.

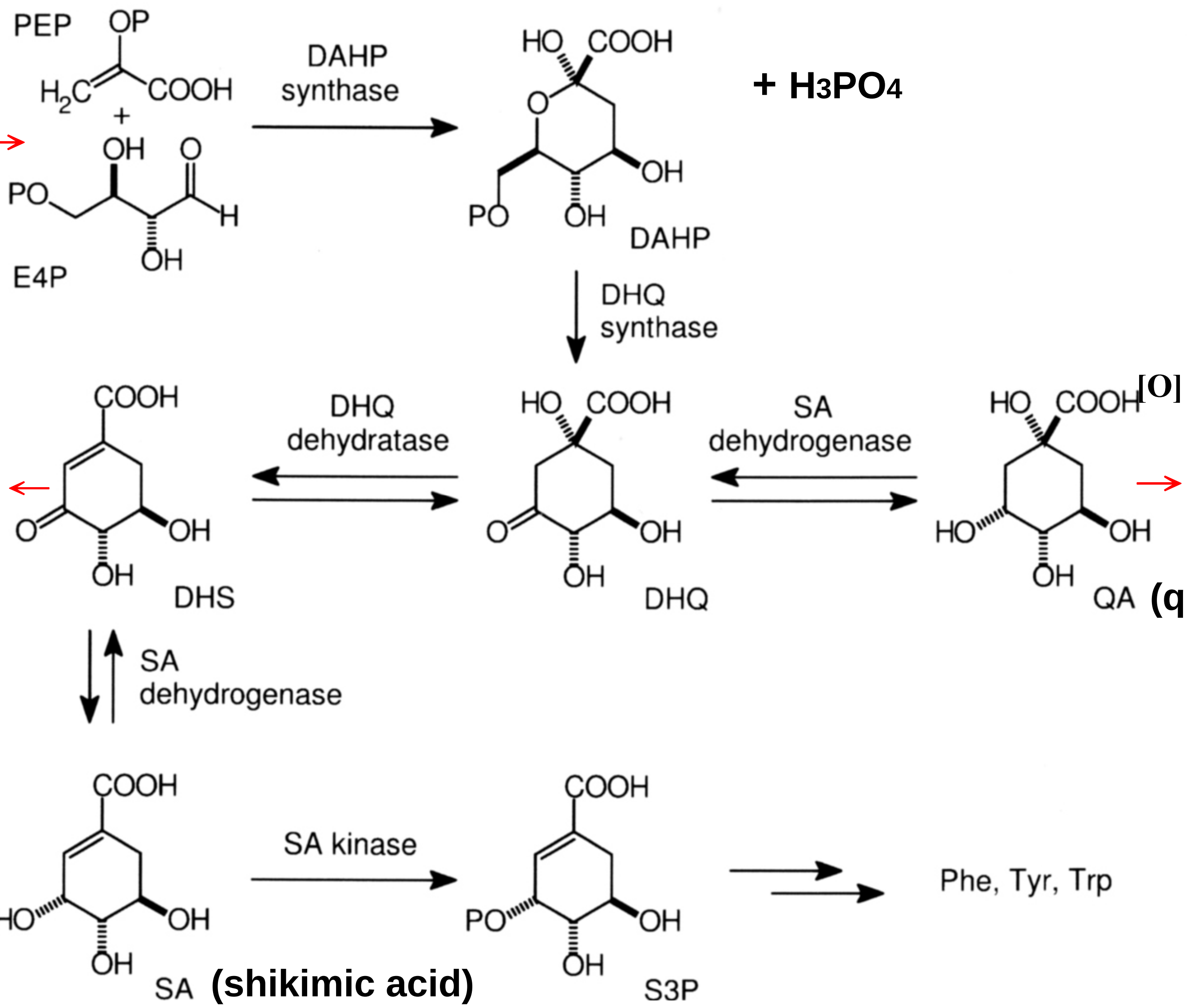
Conversion of cellulose to hexitols catalyzed by ionic liquid-stabilized Ru nanoparticles and a reversiblebinding agent

Zhu, et al., *ChemSusChem* **2010**, *3*, 67-70





Glucose to other chemicals



Glucose →

+ H_3PO_4

[O]

Catechol ← ←

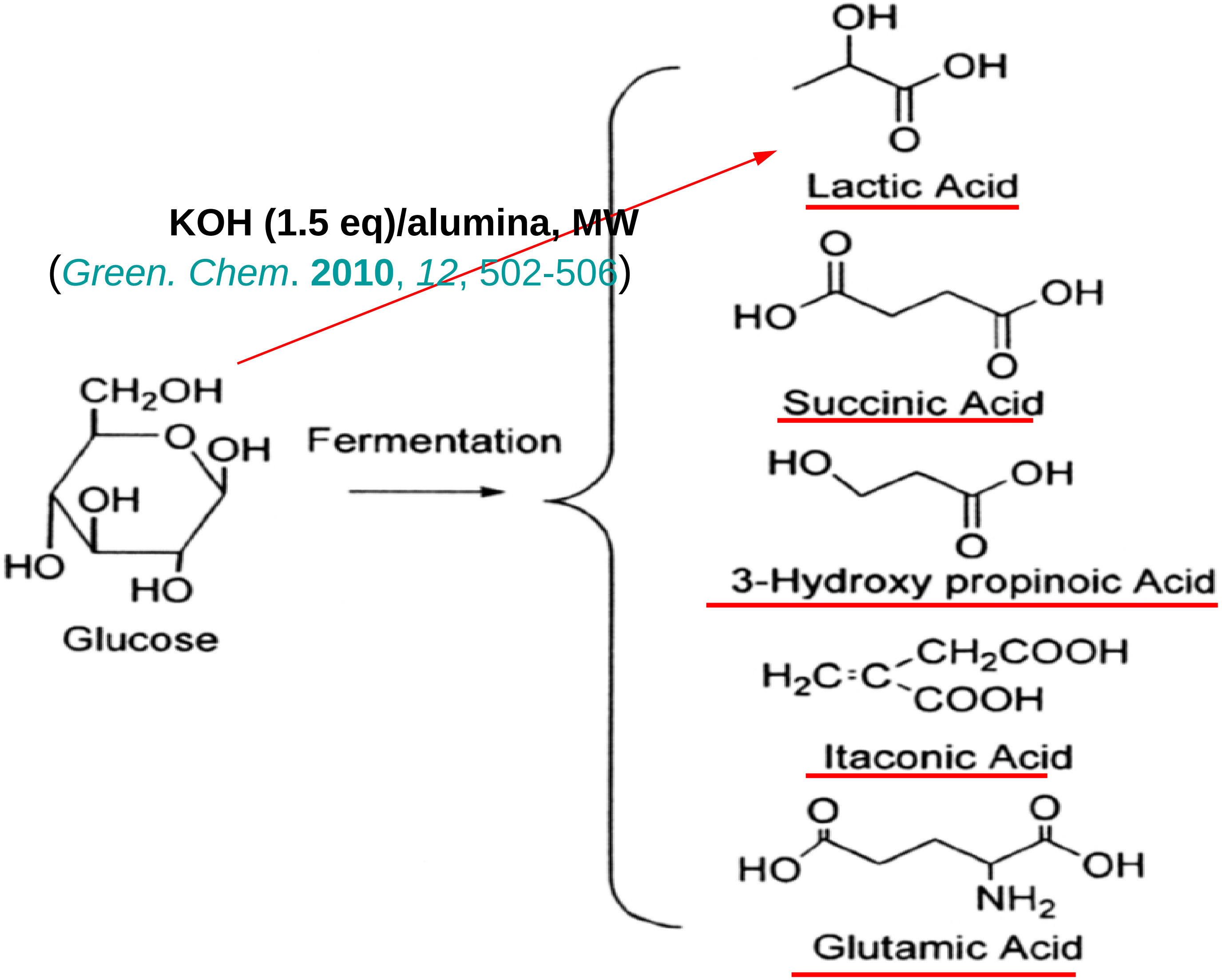
→ **hydroquinone**

(quinic acid)

(shikimic acid)

Darths and Frost (MSU), PGCC Award, 1998

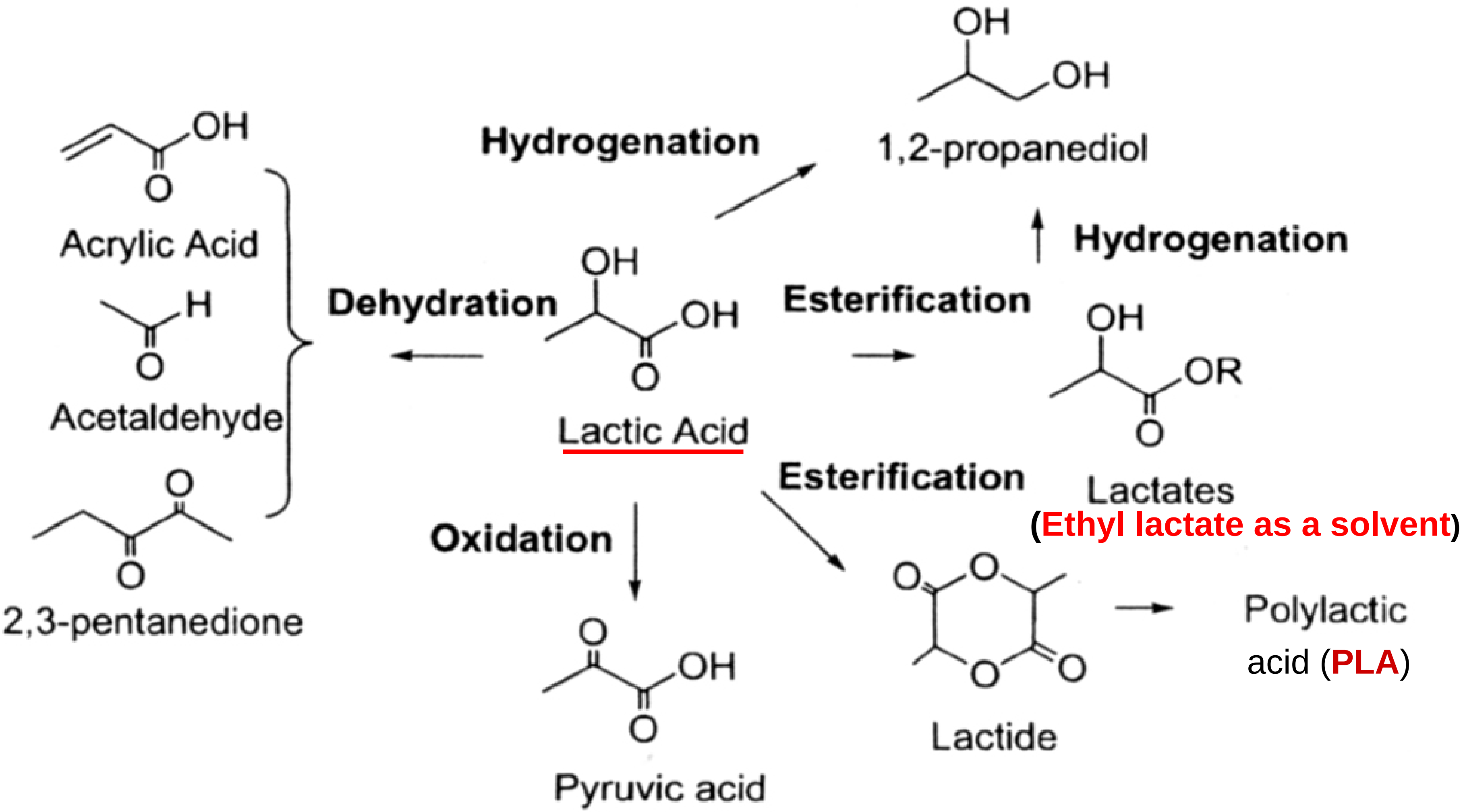
More from fermentation of glucose



KOH (1.5 eq)/alumina, MW

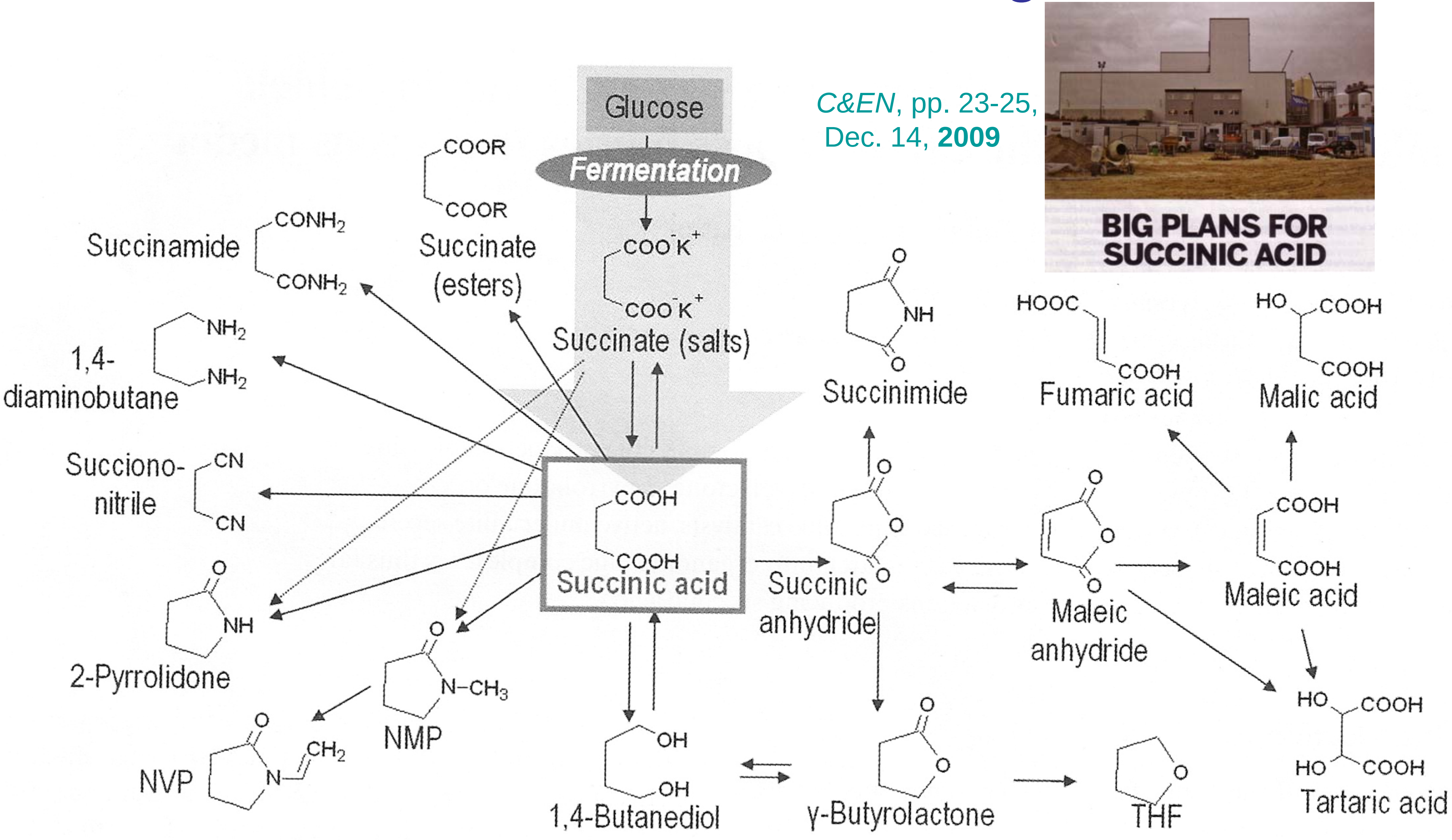
(*Green. Chem*. **2010**, *12*, 502-506)

Important chemicals from lactic acid



(Ethyl lactate as a solvent)

Succinic acid as C-4 building block



BIG PLANS FOR SUCCINIC ACID

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

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

Top chemical opportunities from carbohydrates

DOE(USA, 2004)

Succinic, fumaric and malic acids
2,5-Furandicarboxylic acid (FDCA)
3-Hydroxypropionic acid
Aspartic acid
Glucaric acid
Glutamic acid
Itaconic acid
Levulinic acid
3-Hydroxybutyrolactone
Glycerol
Sorbitol
Xylitol

Bozell and Peterson (suggested 2010)

Ethanol
Furans (Furfural, HMF, FDCA)
Glucerol and derivtives
Biohydrocarbons (including isoprenes)
Lactic acid
Succinic acid
Hydroxypropionic acid/aldehyde
Levulinic acid
Sorbitol
Xylitol

Green Chem. **2010**, *12*, 539-554

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

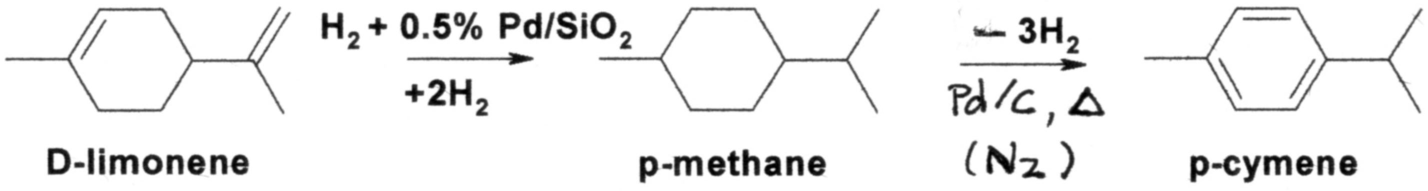
a solvent

an important intermediate chemical in the fragrance industry

an intermediate

a *p*-cresol intermediate

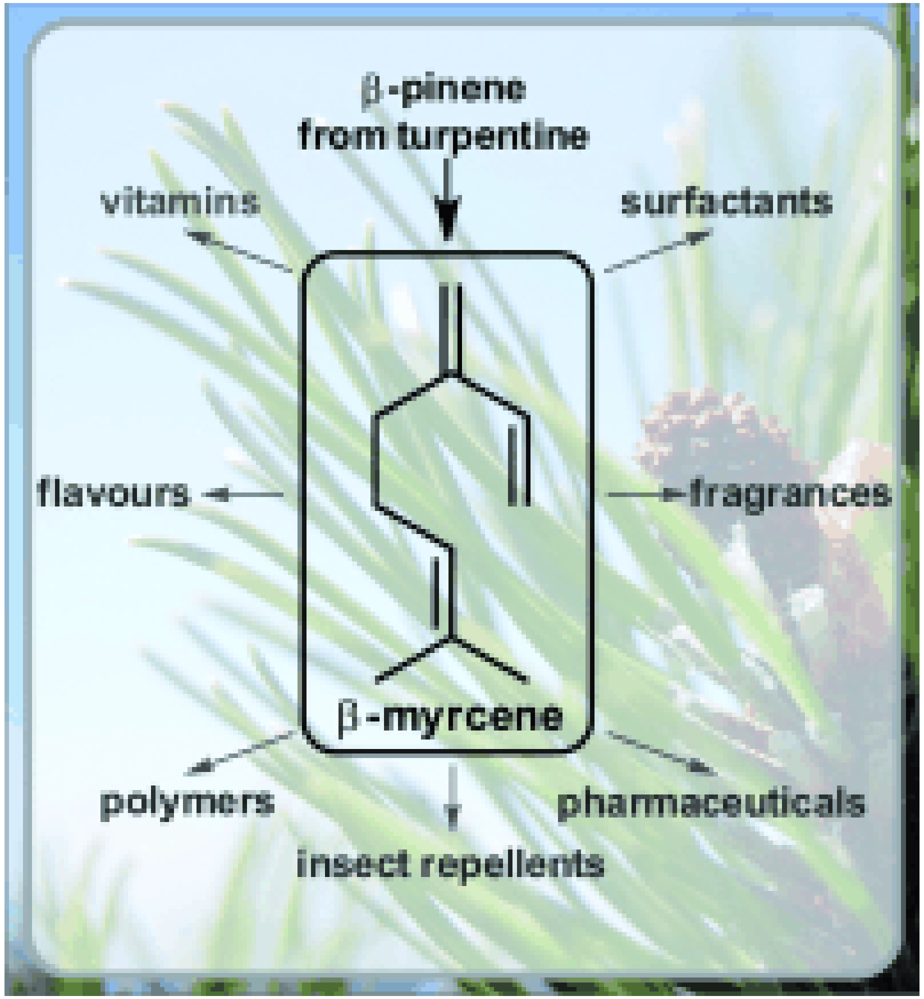
a raw material for synthesis of non-nitrated musks



→ **terephthalic acid**

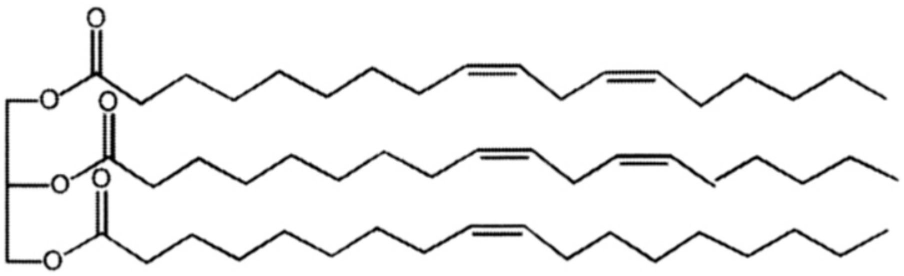
1,8-Cineole → p-cymene + H_2 (*Green Chem*. **2010**, *12*, 77-80)

Myrcene as a Natural Base Chemical in Sustainable Chemistry

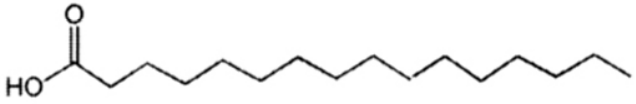


Behr and Johnen, *ChemSusChem* **2009**, *2*, 1072-1095

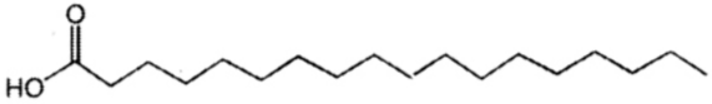
Fats and oils (Triglycerides)



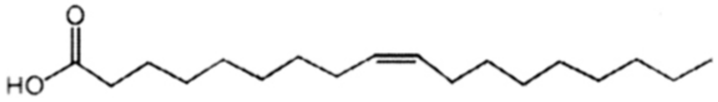
Soybean oil is a statistical mixture of glycerol esters of palmitic acid (10%), stearic acid (3%), oleic acid (23%), linoleic acid (55%), and linolenic acid (9%).



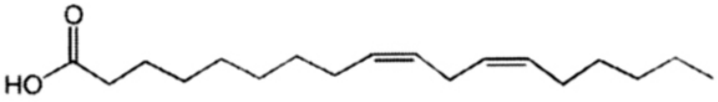
Palmitic acid



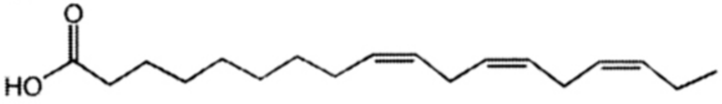
Stearic acid



Oleic acid



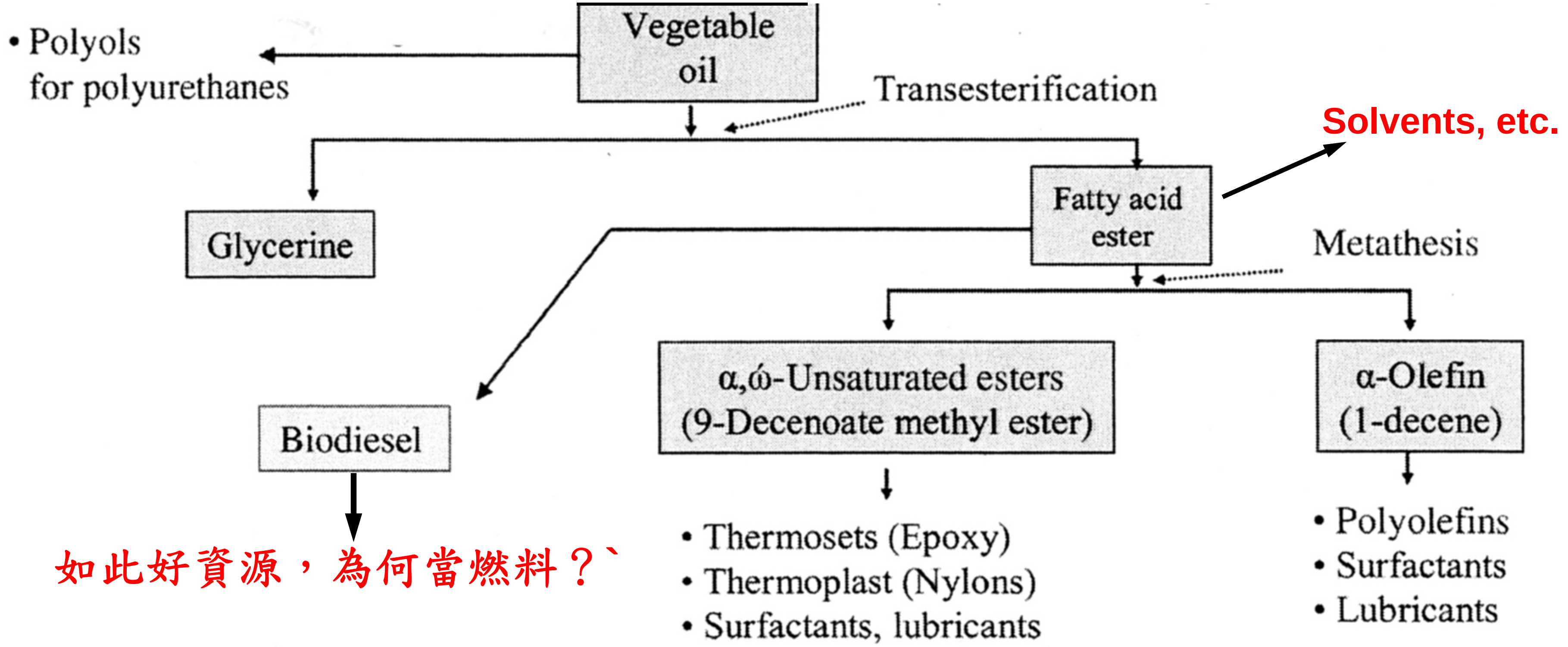
Linoleic acid



Linolenic acid

and glycerol (glycerin) $CH_2(OH)CH(OH)CH_2OH$

Bio-refinery of vegetable oils



Vegetable oil

- Polyols
  for polyurethanes

Transesterification

Glycerine

Fatty acid ester

Solvents, etc.

Metathesis

Biodiesel

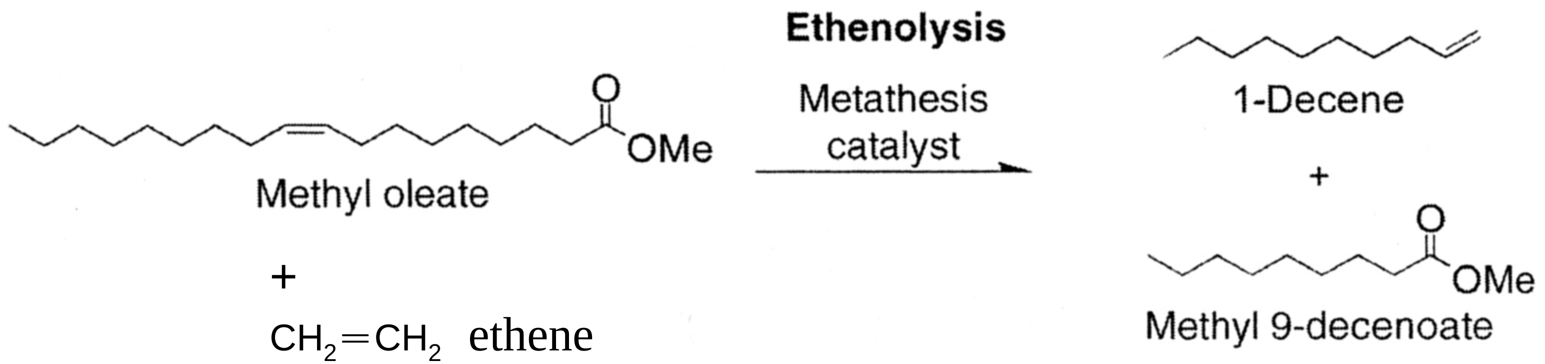
如此好資源，為何當燃料？`

α,ώ-Unsaturated esters (9-Decenoate methyl ester)

- Thermosets (Epoxy)
- Thermoplast (Nylons)
- Surfactants, lubricants

α-Olefin (1-decene)

- Polyolefins
- Surfactants
- Lubricants

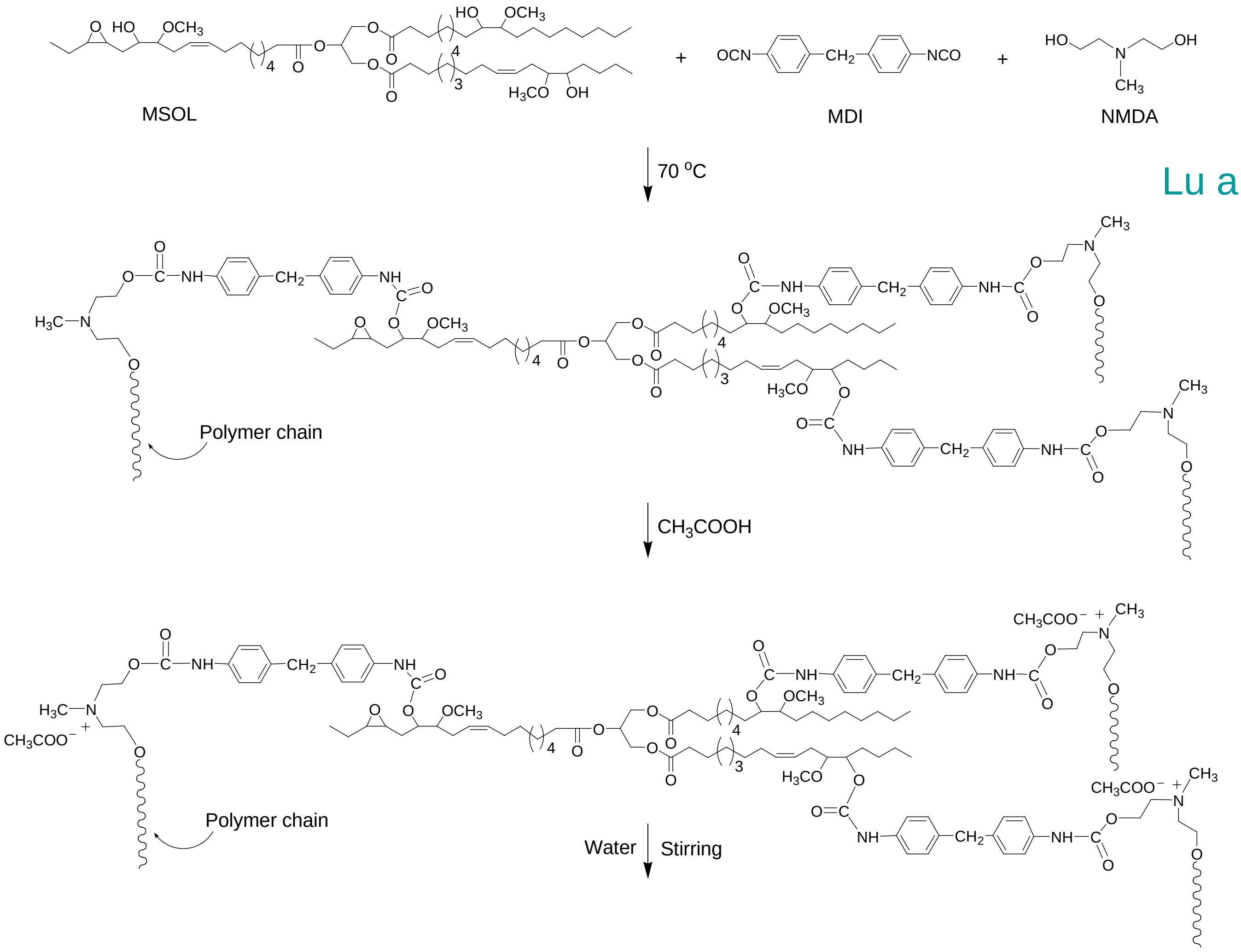


\+

$CH_2=CH_2$ ethene

Aqueous Cationic PU Dispersions from Vegetable Oils

The resulting environmentally friendly PUDs exhibit excellent physical properties, indicating great promise for use as adhesives, plastics, and coatings.



Lu and Larock, *ChemSusChem* **2010**, *3*, 329-333

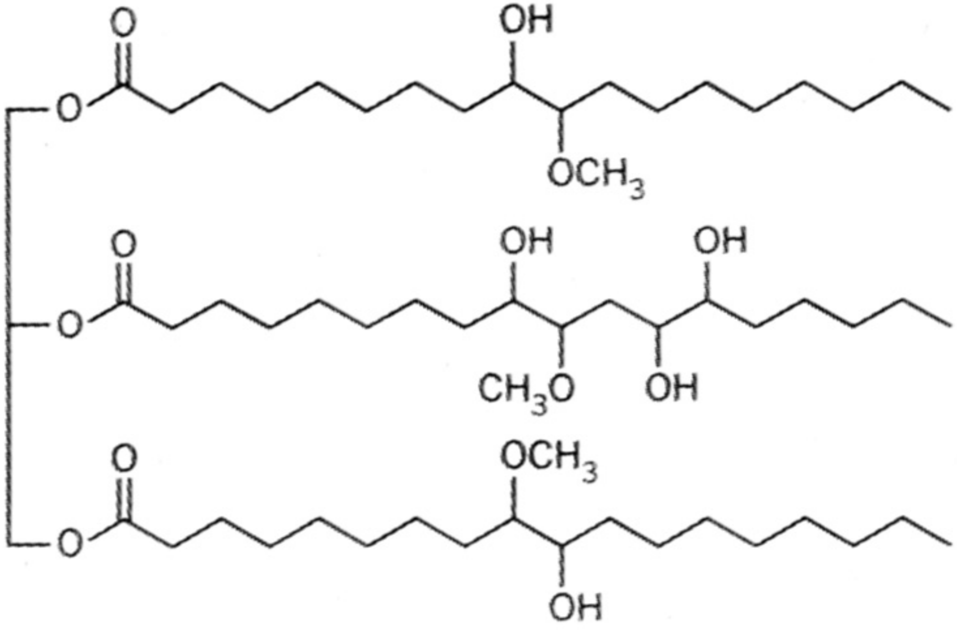
Vegetable Oil-Based Aqueous Cationic Polyurethane Dispersions

2007 PGCC Designing Greener Chemicals Award

BiOH™ Polyols

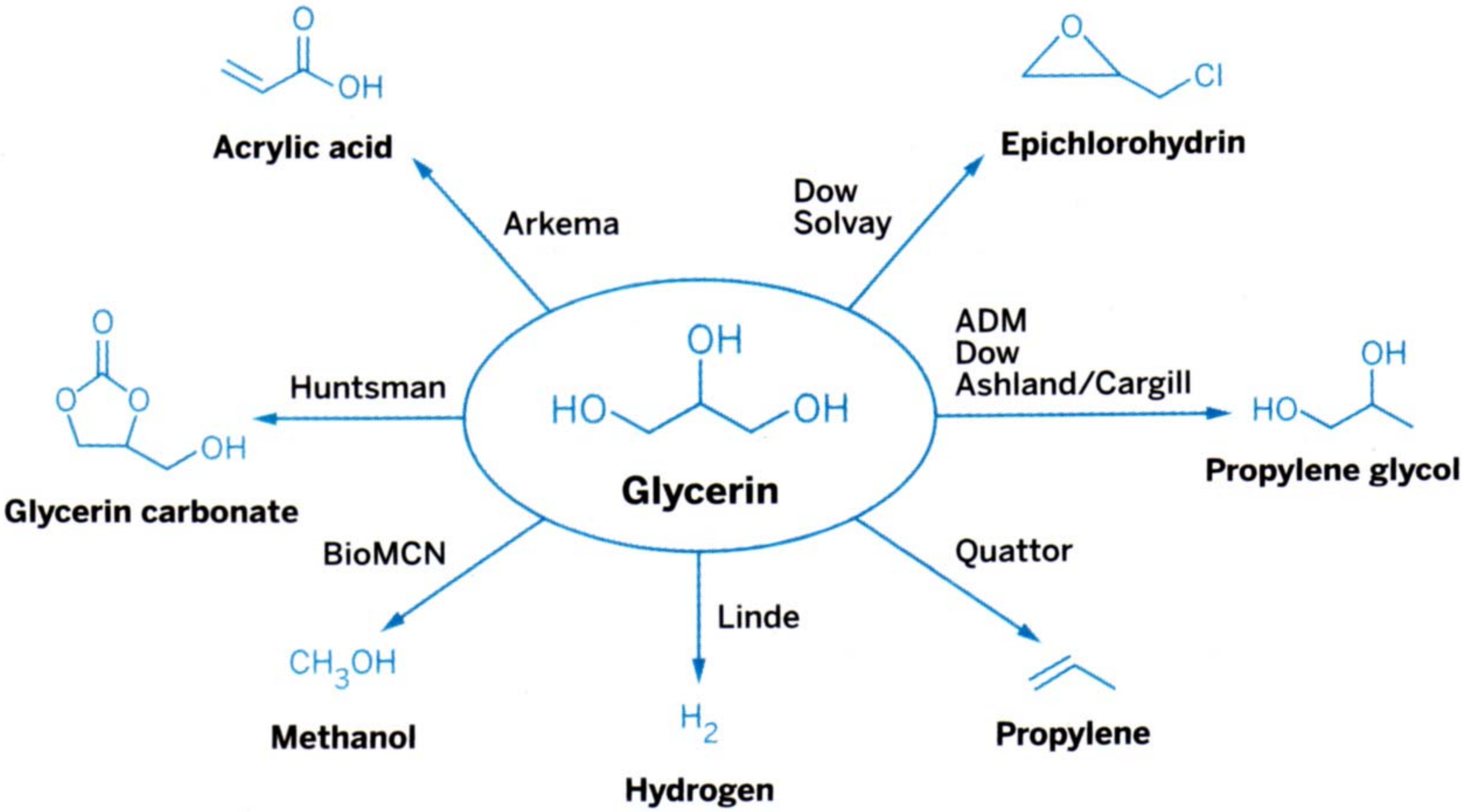
Cargill, Incorporated

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 %.

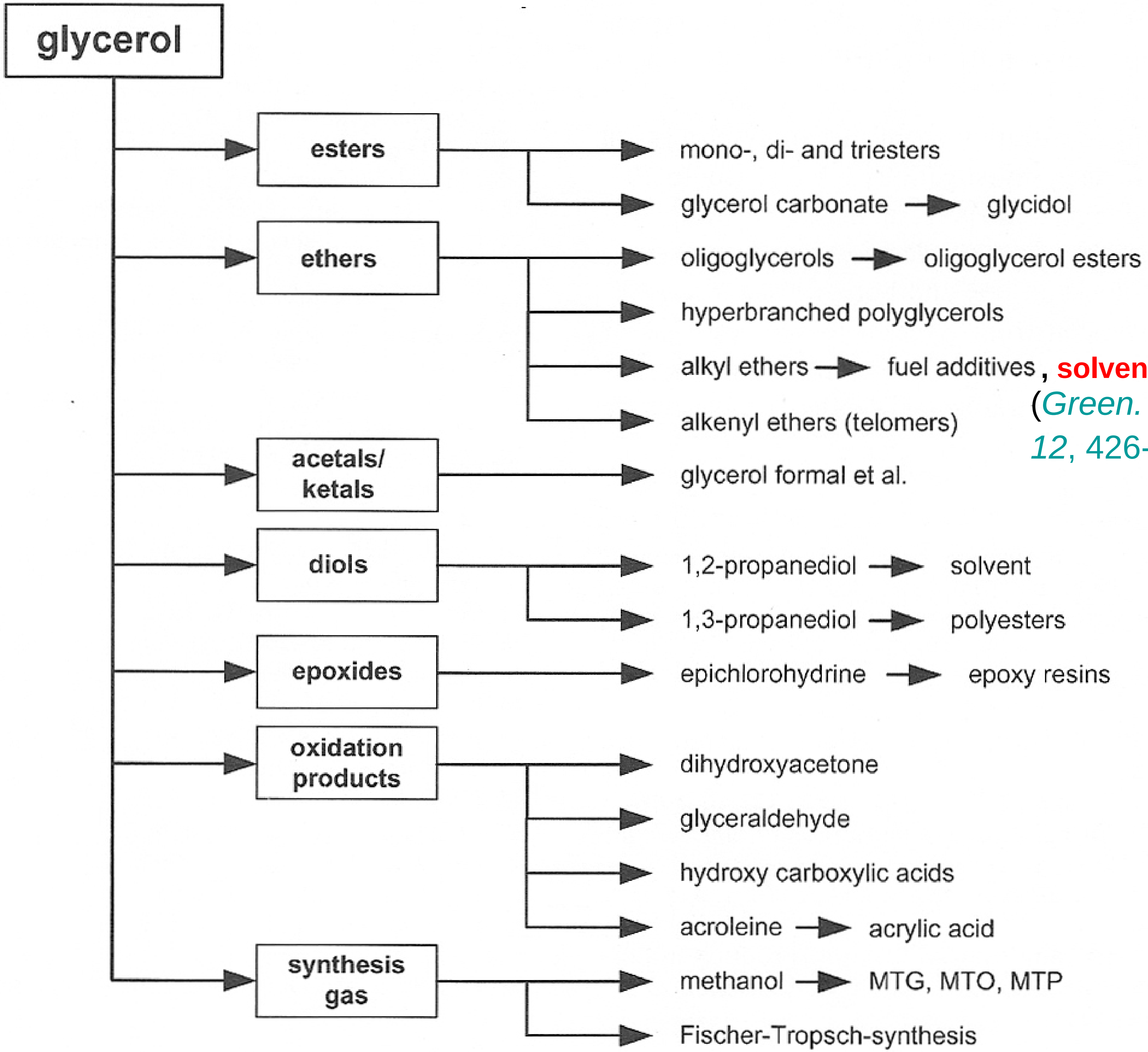


The use of fatty acids and glycerol

- 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)

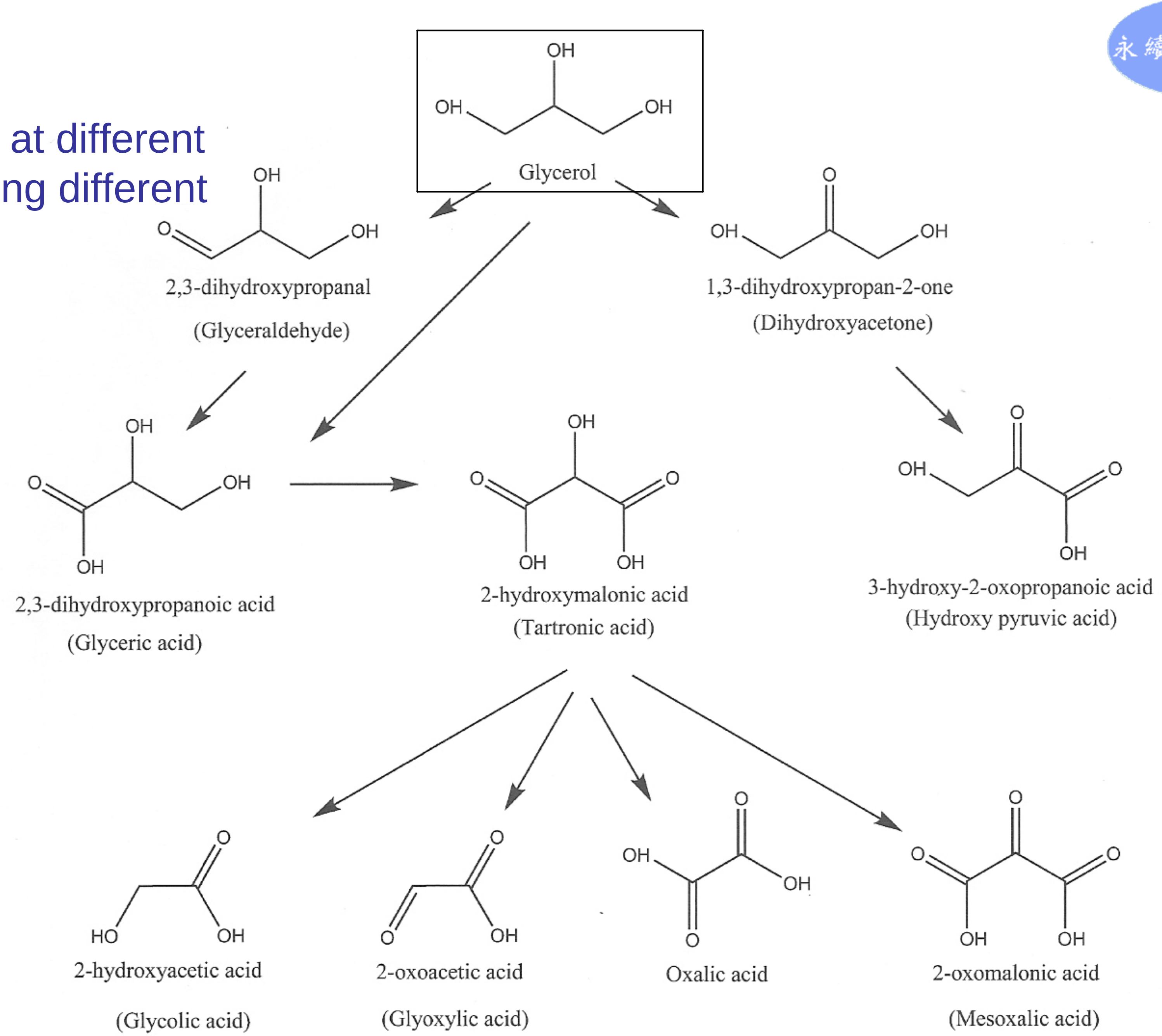


glycerol

- **esters**
  - mono-, di- and triesters
  - glycerol carbonate → glycidol
- **ethers**
  - oligoglycerols → oligoglycerol esters
  - hyperbranched polyglycerols
  - alkyl ethers → fuel additives, **solvents, etc.**
  - 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

(*Green. Chem.* **2010**, *12*, 426-434)

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

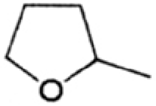
Biobased Propylene Glycol and Monomers from Natural Glycerin

Innovation and Benefits:

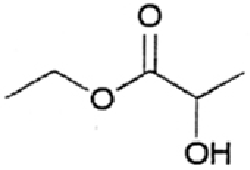
Professor Suppes (U. Missori-Columbia) developed an inexpensive method to convert waste glycerin, a byproduct of biodiesel fuel production, into propylene glycol, which can replace ethylene glycol in automotive antifreeze. It can help biodiesel become a cost-effective, viable alternative fuel…

(glycerol → 1,2-propanediol**)**

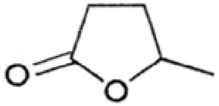
Solvents from renewable resources



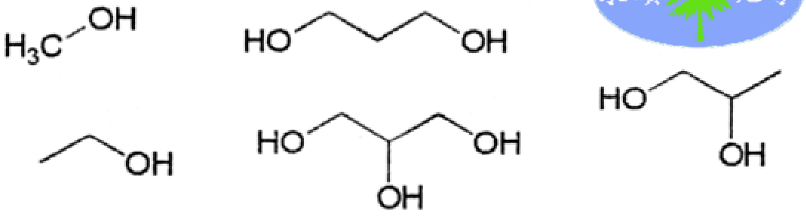
2-MeTHF



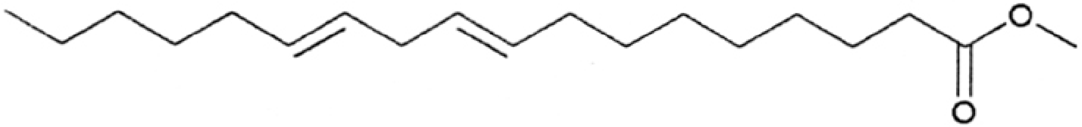
Ethyl lactate



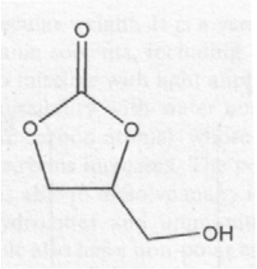
γ -Valerolactone



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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