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]。

永續化學溶劑的一些新發展

劉廣定
(ktliu@ntu.edu.tw)

November 1, 2012

永續發展觀念之形成

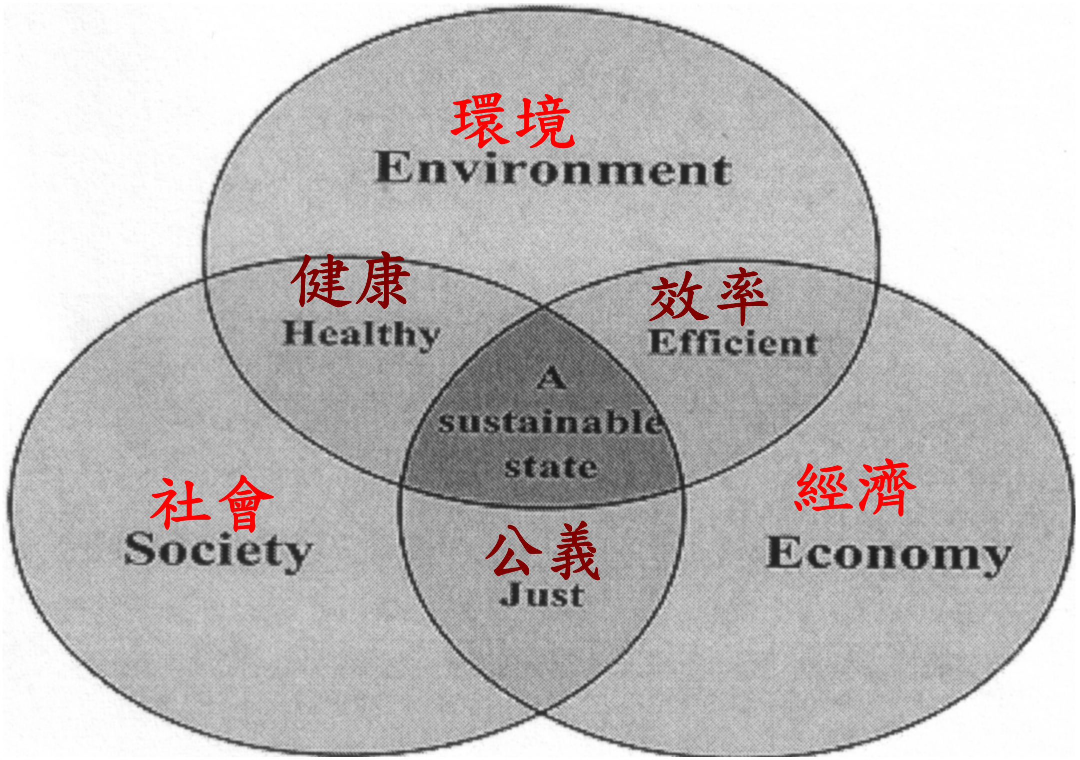
近年來，永續發展（sustainable development）是國際上逐漸形成之重要思潮與具體行動。據1987年聯合國世界環境與發展委員會（WCED）報告書之定義：**能滿足當代所需但不損再及後代滿足其所需之發展**稱為**永續發展**。

1992年六月，聯合國在巴西召開首屆「環境與發展」會議，議定「廿一世紀待辦事項」（Agenda 21）40章。界定了「永續發展」為**人類兼顧經濟成長、生態環境與社會責任三基柱的發展**，以及其發展原則。

1993年聯合國成立永續發展委員會,宣導加強認識自然,保護環境之觀念外,並採積極的態度，以創新之發明與設計來促成世界進步，俾使環境、經濟和社會資源得以同時持續發展。

永續發展
Sustainable development

2005年聯合國高峰會再次強調經濟永續、社會永續和環境保護三者之間相互依賴與支援的重要。藉由保護與發展相輔相成，世界將可永續。



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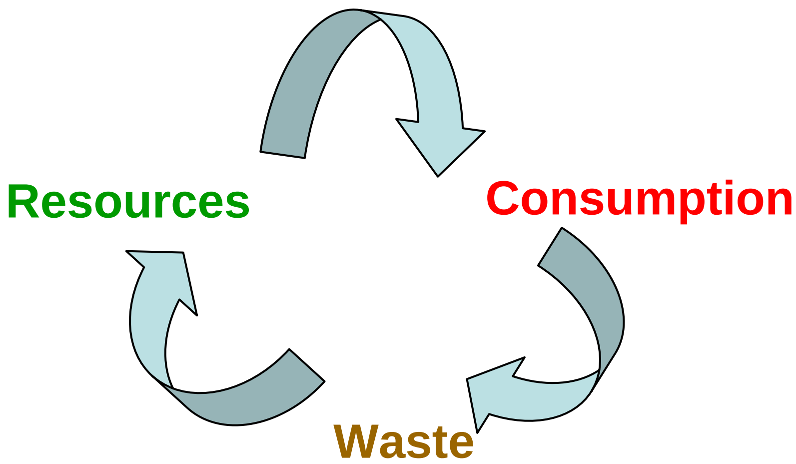
資源與環境的觀點

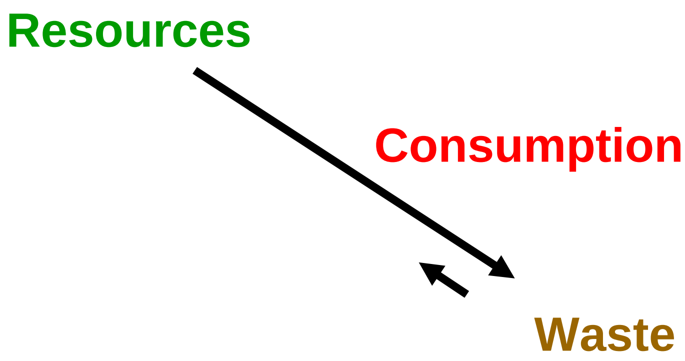
Nature

a cycle



Industrial Society

the natural cycle disrupted



We are using resources and creating waste much faster that the earth can take our wastes and convert them back into resources.

我們消耗地球資源製造廢棄物已比地球將廢棄物轉成資源快得多 — 地球資源將愈來愈不足，環境品質將愈來愈差

化學化工的基礎觀點：環境因數

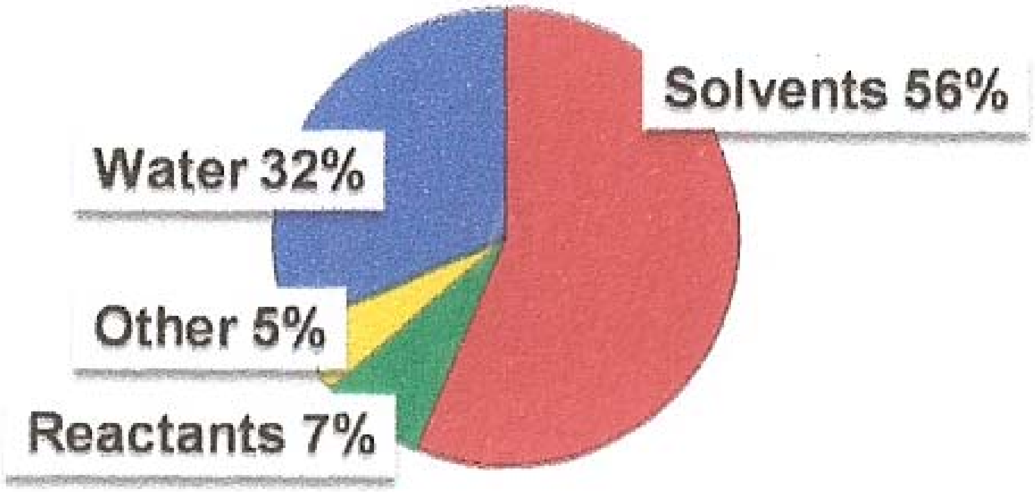
E-factor = kg(副產物+廢棄物)/kg(主產物)

工業製程	每年產量（噸）	E 因數
原油煉製	$10^6 \sim 10^8$	小於0.1
工業化學品	$10^4 \sim 10^6$	小於1～5
精緻化學品	$10^2 \sim 10^4$	5 到大於50
醫藥化學品	$10^1 \sim 10^3$	25到大於100

1992年荷蘭Delft技術大學Sheldon教授之統計(*Chemtech* **1994**, *24*, 38-47)

Environmental impact of manufacturing processes of active pharmaceutical Ingredients

A 2007 study showed the median amount of **materials used to make 1 kg of API was 46 kg**, in which 56% of the mass used was solvent. That is, 22 kg of solvents are needed to make 1 kg of API. **E = 45**



(*Org Process Res Dev*. **2007**, *9*,1173-1283)

永續化學

Green / sustainable chemistry is the invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances. (OECD Workshop on Sustainable Chemistry, 1998)

2020 Sustainability Goals

Zero waste: eliminate the concept of waste in product, process, material and energy.

Zero toxic substances: eliminate substances known or suspected to be harmful to human health or the health of biological systems.

100% Closed loop processes: take 100% responsibility for our products at all stages of our product and process lifecycle.

Sustainable growth and profitability: create an economy the planet is capable of sustaining indefinitely.

(Zero Waste Alliance, 2001)

永續的化學與化工

- 「節能、減碳」與「環境保護」是不夠的至少須做到「節能、減廢」
- 反應方法、實驗原則、試劑、溶劑、觸媒等都能盡量配合永續化學與永續工程的原則
- 準則是以「減」求「增」—增產、增效、增利…
- **Reduce**: **Cost** **Non-renewables**
  Energy **Risk**
  Environmental impact **Space**
  Hazards **Time**
  Materials **Waste**
  ……
- 改進或創新製程以達目的(Process optimization for energy saving and waste reduction)

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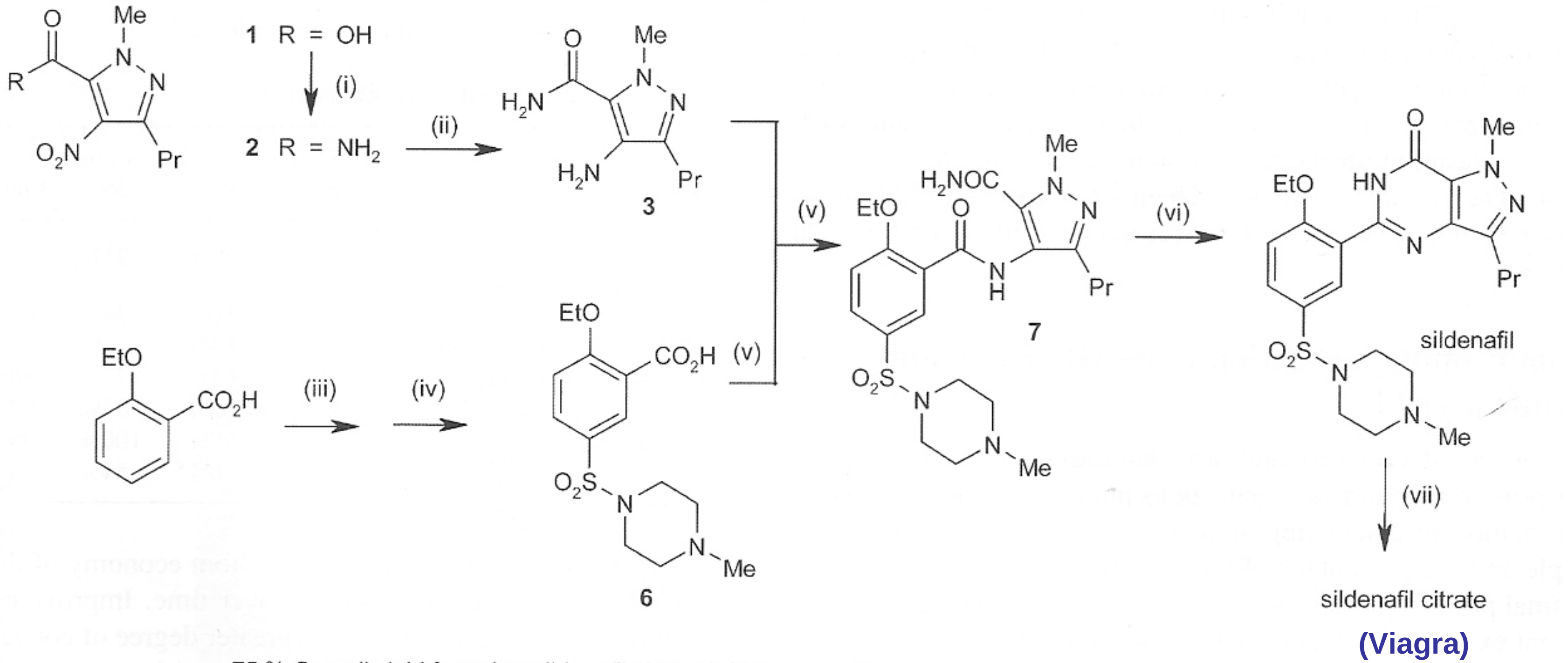
Sildenafil citrate process

2003 CRTSTAL Faraday Award

P. J. Dunn, *et al.* *Green Chem*., **2004**, *6*, 43-48; *Org. Proc. Res. Dev*., **2005**, *9*, 88-97

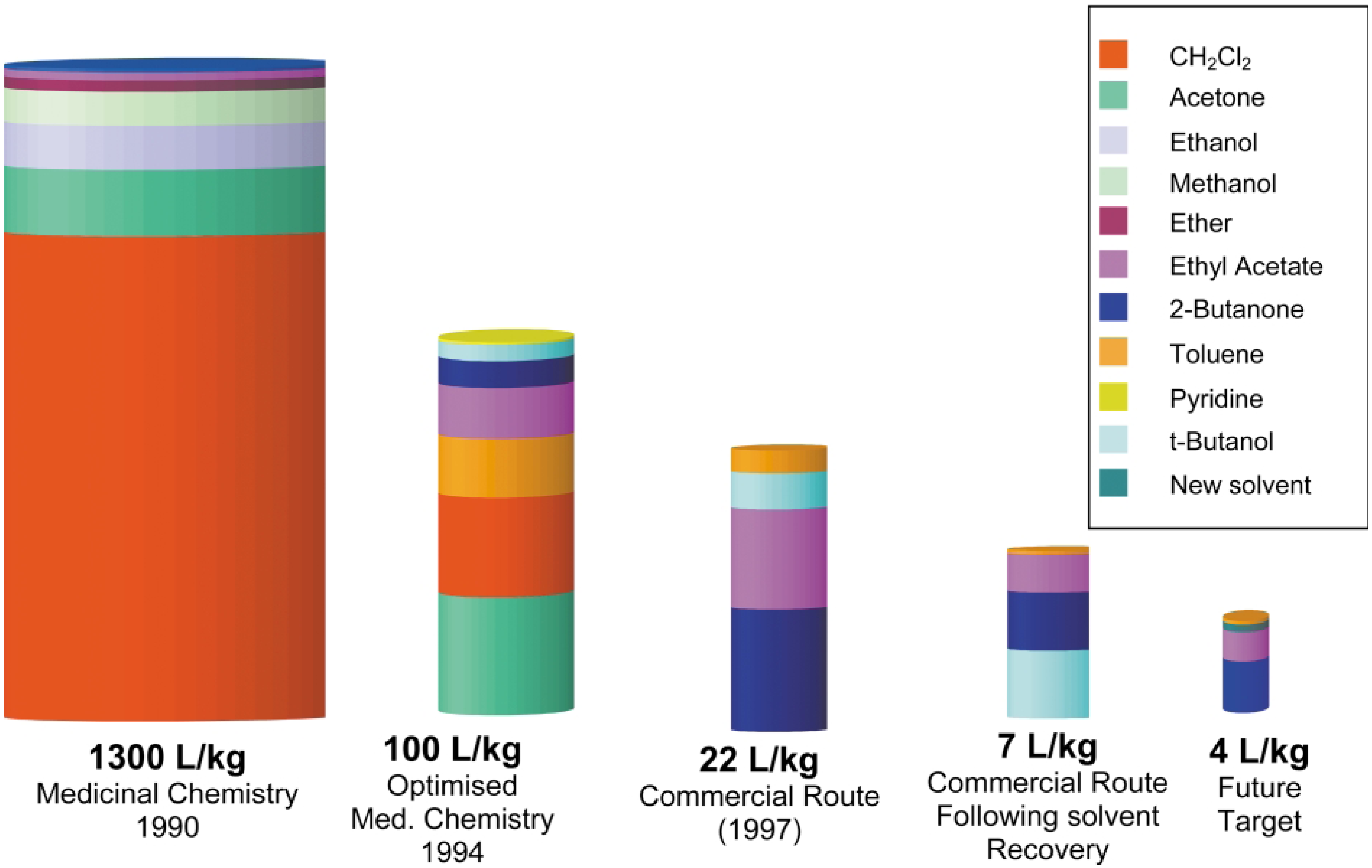
The development of the sildenafil citrate process is outlined. The E-factor for the final process is 6 Kg waste per kilogram of product.



75 % Overall yield from **1** to sildenafil citrate (1997 process)

(i) Step 1, $SOCl_2$, DMF (cat.), Δ toluene; NH_3 (aq) (92%) (ii) Step 3a, H_2 Pd/C EtOAc (100%) (iii) Step 2, $ClSO_3H$, $SOCl_2$ 25°C (iv) Step 2, *N*-methylpiperazine, water, 25°C then neutralisation (v) Step 3b, **6** + CDI, EtOAc, add **3** (90 %) (vi) Step 4, $KOBu^t$, Δ *t*-BuOH, (92 %) (vii) Step 5, citric acid, 2-butanone (99 %).

Solvents used in the sildenafil citrate process



Before 2004

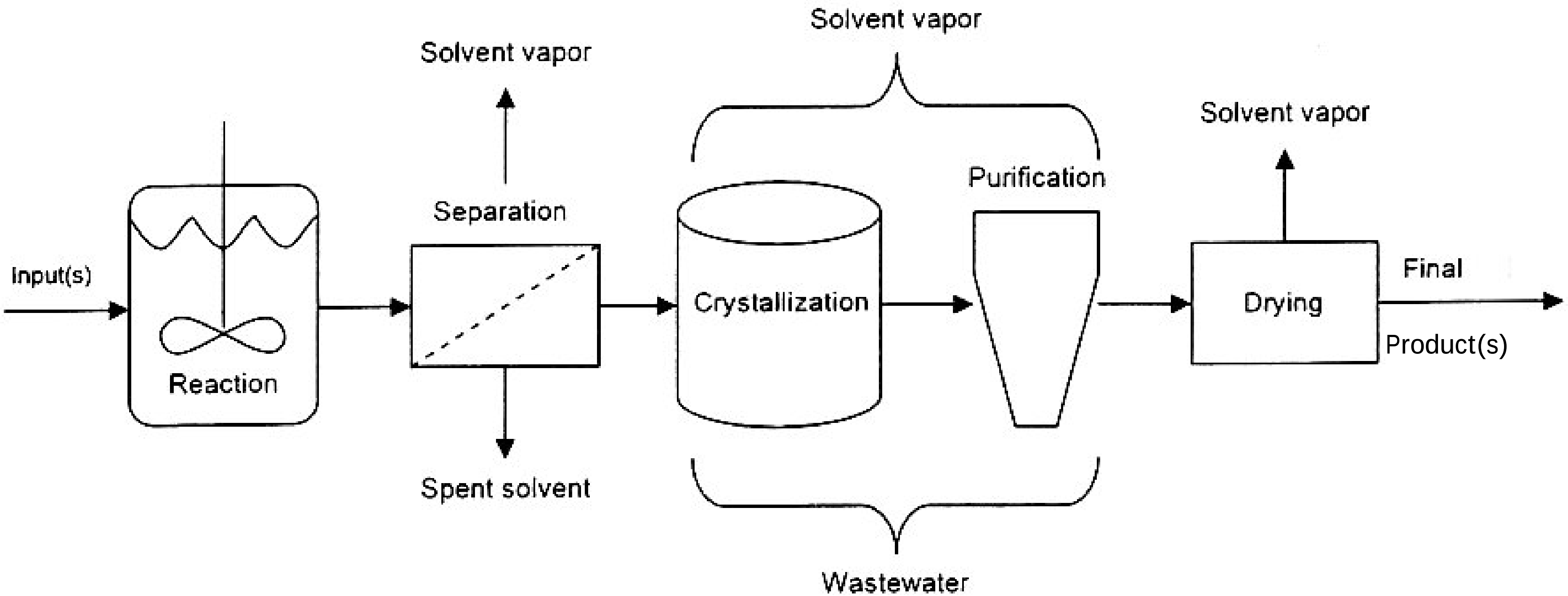
A variety of approaches

- **Methods of chemical activation**: thermo-, photo-, electro-, high pressure, ultrasound, microwave, mechano-chemistry
- **More effective methodologies:** multicomponent reactions, new catalysts, continuous flow and micro-reactors, modifying procedure
- **Alternative solvents**：replacement of petroleum-based, and volatile organic compounds (VOCs), switchable systems, solvent-less procedure
- Methods of recovery
- New synthetic pathways, etc.

Cl-free synthesis: *Pure Appl. Chem*. **2012**, *84*, 411-860

多數化學反應在溶劑中進行

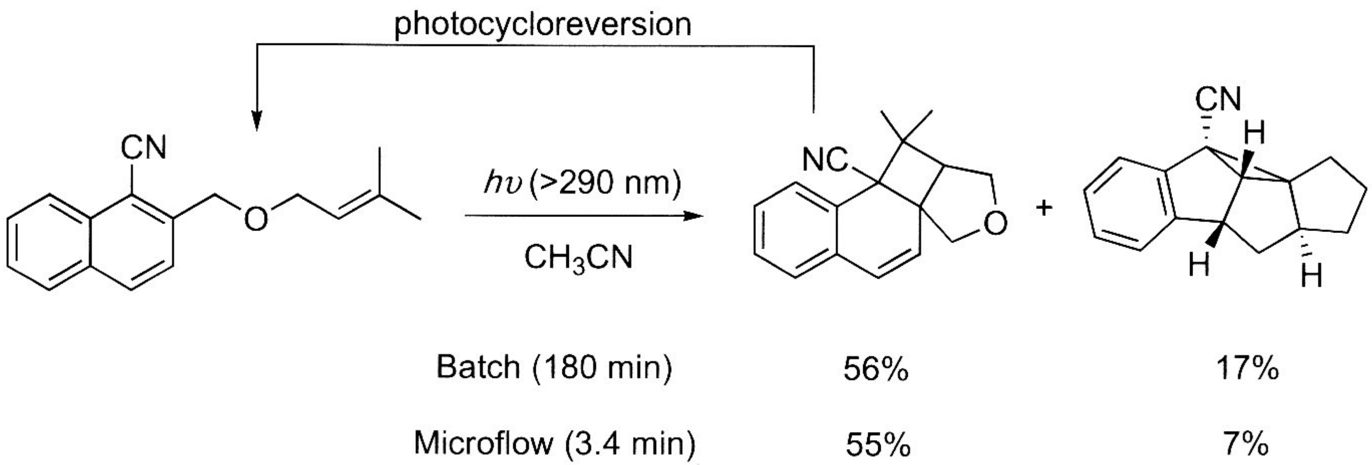
A typical batch operation

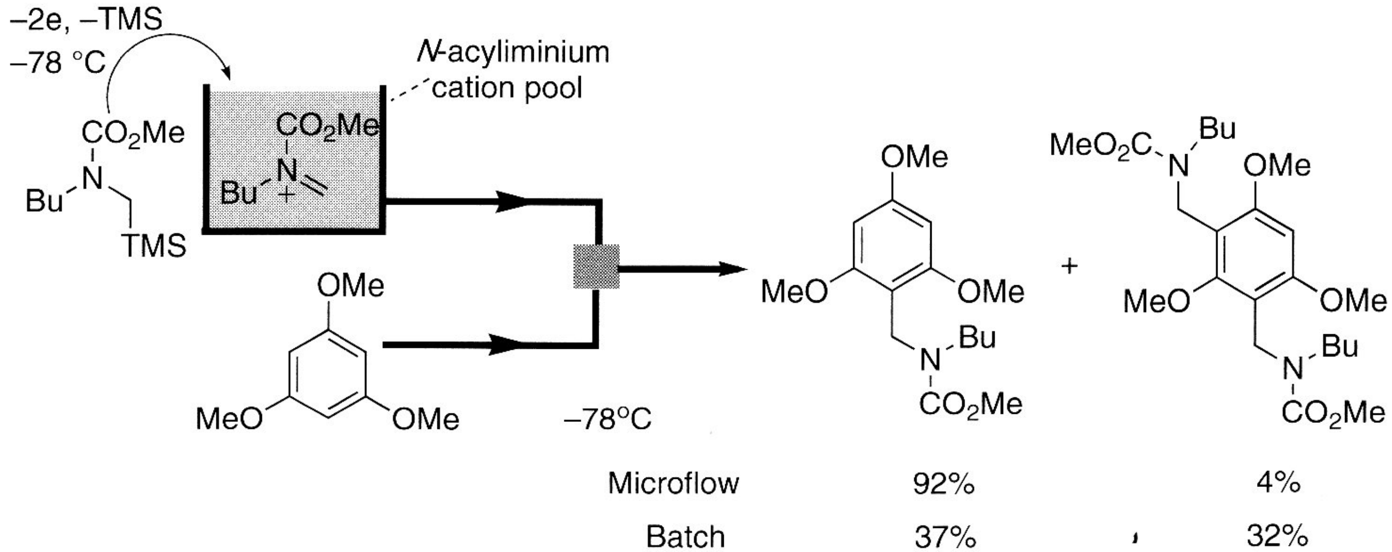


連續流動製程必需溶劑

溶劑回收方法之改進

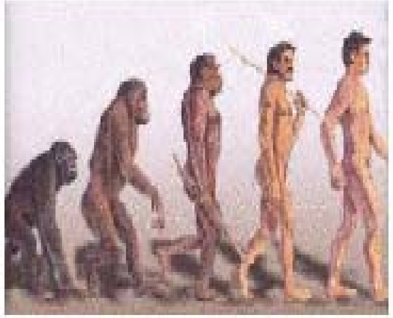
Continuous flow and microreactors

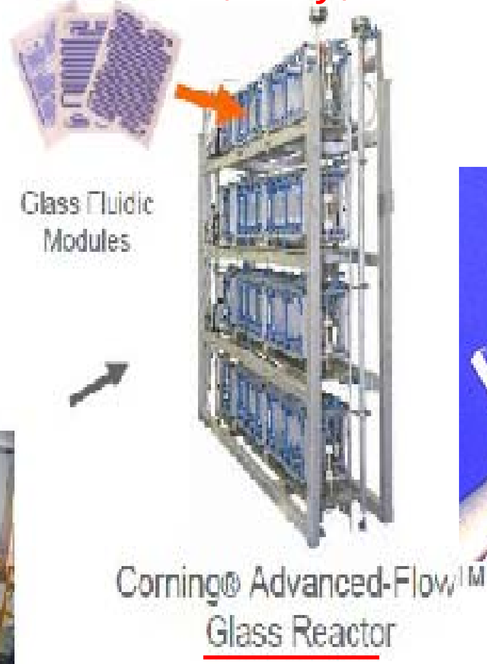




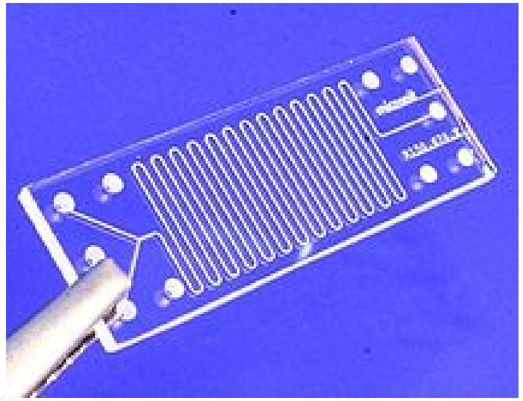
Microreactors in Organic Synthesis and Catalysts, **2008**, Wiley-VCH,p. 72, p. 79

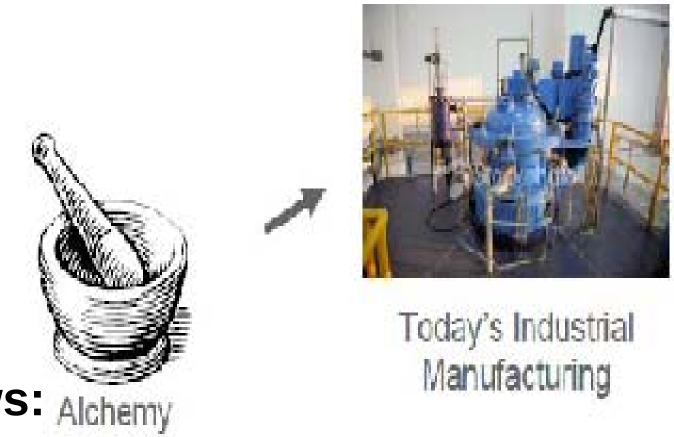
Corning Advanced-Flow Reactor, May, 2009





Channel with 150 x 150 μm (Wikipedia)





Georgia Tech to Use Corning Advanced-Flow Reactor in Synthesis Research since April, 2010

Ceramic reactor, announced June, 2011

Some reviews:

- **Cross-coupling in flow** (*Chem. Soc. Rev*., **2011**, *40*, 5010–5029)
- **Synthesis using Flow Microreactors** (*ChemSusChem* **2011**, *4,* 331-340)
- **A Versatile Lab to Pilot Scale Continuous Reaction System for Supercritical Fluid Processing** (*Org. Process Res Dev*. **2011**, *15*, 1275-1280)
- **Continuous flow reactors: a perspective** (*Green Chem.* **2012,** *14***,** 38-54)
- **Continuous reactions in supercritical CO_2** (*Chem. Soc. Rev*. **2012**, *41*, 1428-1436)
- **Microwave-assisted continuous flow synthesis on industrial scale(***Green Process. Syn.* **2012,** *1,* 281-290)

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Special issue:

Flow Chemistry

(pp. 213-350)

Special issue:

Continuous processes

(pp. 811-818; 844-1153)

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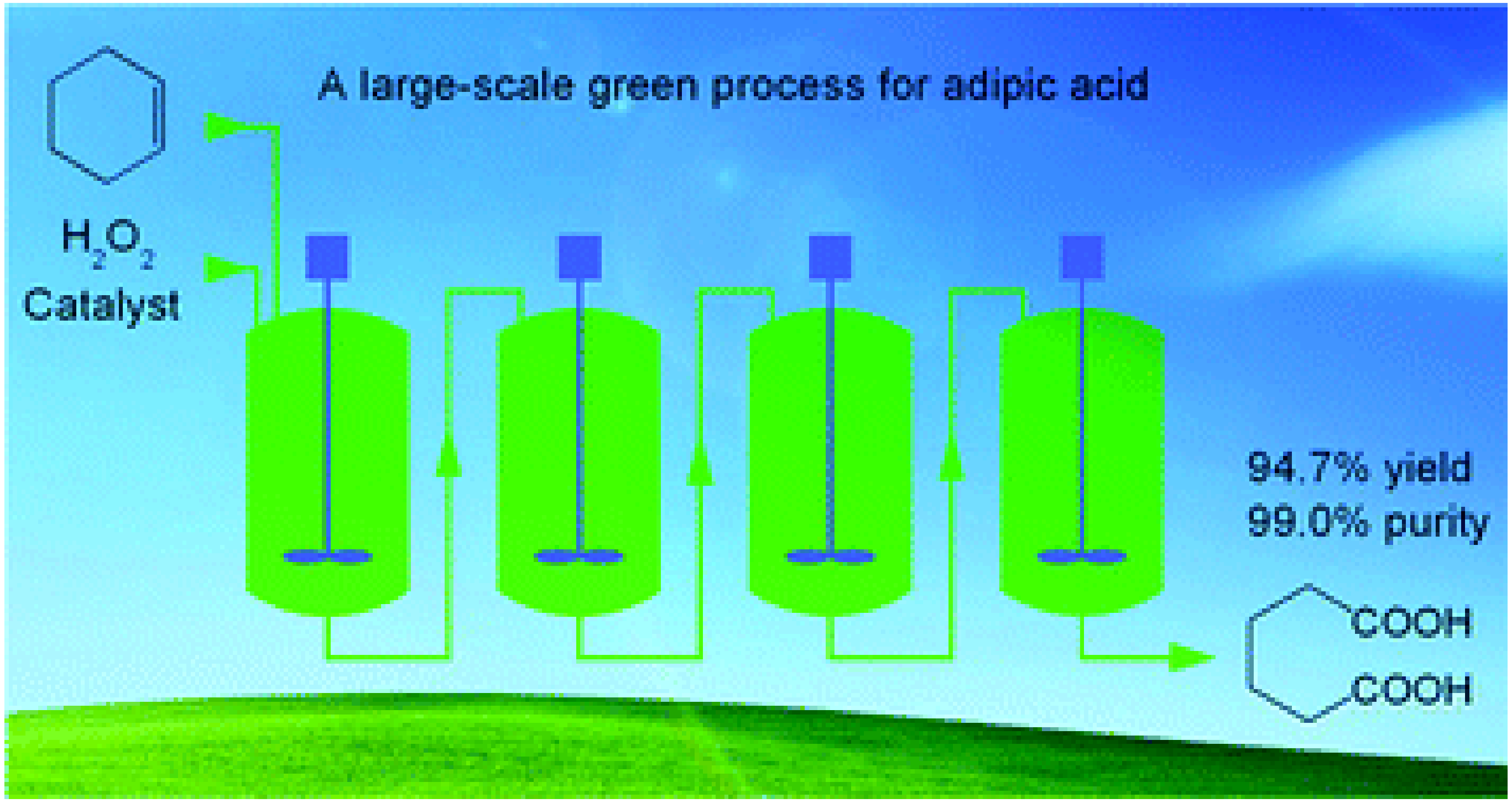
A large-scale continuous-flow process with four 5000 L stirred tank reactors (CSTR) for production of adipic acid *via* catalytic oxidation of cyclohexene has been developed. (Zhengchou University)



Green Chem., 2012, **14**, 2868-2875

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Safety of solvents---NFPA 704

- **NFPA 704** is a standard maintained by the U.S.-based National Fire Protection Association. It defines the colloquial "**fire diamond**" used by emergency personnel to quickly and easily identify the risks posed by nearby hazardous materials. This is necessary to help determine what, if any, specialty equipment should be used, procedures followed, or precautions taken during the first moments of an emergency response.
- For example, cyclohexane

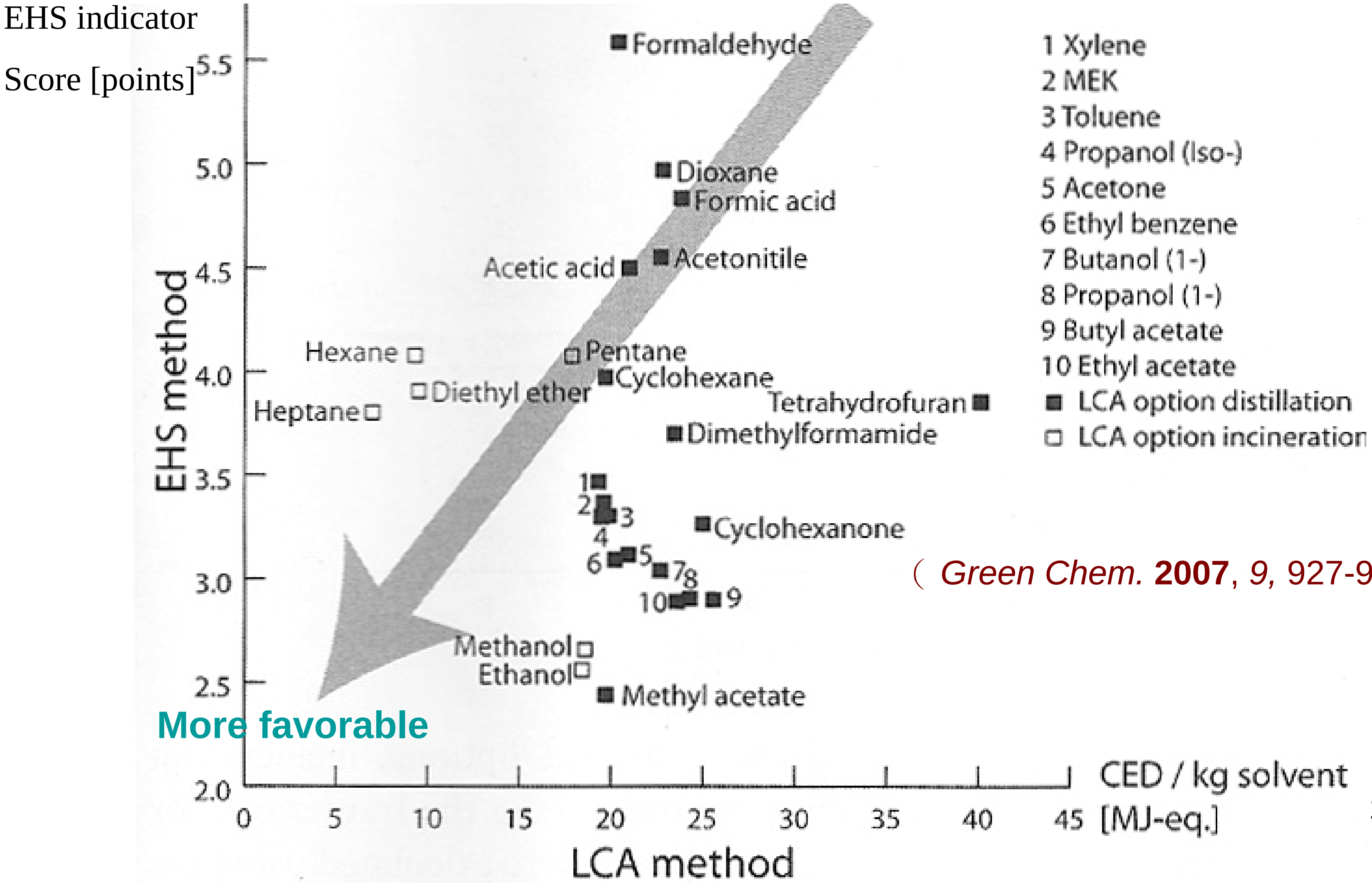
What does it mean?

Blue: health; **Red**: flammability; **Yellow**: reactivity; **White**: special

Numbers: 4, 3, 2, 1, 0

A comprehensive framework for the environmental assessment of 26 solvents

Environmental-health-safety and Life cycle assessment



（*Green Chem.* **2007**, *9*, 927-934）

Rowan solvent greenness index

(Slater and Savelski)

- Inhalation Toxicity – Threshold Limit Value (TLV)
- Ingestion Toxicity
- Biodegradation
- Aquatic Toxicity
- Carcinogenicity
- Half-Life
- Ozone Depletion
- Global Warming Potential
- Smog Formation
- Acidification
- Soil Adsorption Coefficient
- Bioconcentration Factor

(*Chem. Soc. Rev*. **2012**, *41*, 1452-1461)

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Pfizer solvent selection guide

Preferred	Usable	Undesirable
Water	Cyclohexane	Pentane
Acetone	Toluene	Hexane(s)
Ethanol	Methylcyclohexane	Di-isopropyl ether
2-Propanol	TBME	Diethyl ether
1-Propanol	Isooctane	Dichloromethane
	Acetonitrile	Dichloroethane
Ethyl Acetate	2-MeTHF	Chloroform
Isopropyl acetate	THF	NMP
Methanol	Xylenes	DMF
MEK	DMSO	Pyridine
1-Butanol	Acetic Acid	DMAc
t-Butanol	Ethylene Glycol	Dioxane
	Heptane	Dimethoxyethane
		Benzene
		Carbon Tetrachloride

(*Green Chem*. **2008**, *10*, 31-36)

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Pfizer's solvent replacement table

Undesirable solvents	Alternative
Pentane	Heptane
Hexane(s)	Heptane
Di-isopropyl ether or diethyl ether	2-MeTHF or *tert*-butyl methyl ether
Dioxane or dimethoxyethane	2-MeTHF or *tert*-butyl methyl ether
Chloroform, dichloroethane, carbon tetrachloride	Dichloromethane
Dimethyl formamide, dimethyl acetamide, *N*-methylpyrrolidinone	Acetonitrile
Pyridine	Et_3N (if pyridine used as base)
Dichloromethane (extractions)	EtOAc, *tert*-butyl methyl ether, toluene, 2-MeTHF
Dichloromethane (chromatography)	EtOAc/heptane
Benzene	Toluene

Table 1. **Comparison of solvent use in GlaxoSmithKline Pharmaceuticals (GSK) prior to 2000 and in pilot plant processes carried out in 2005**

	2005 rank	1990–2000 rank
2-propanol	1	5
ethyl acetate	2	4
methanol	3	6
denatured Ethanol	4	8
n-heptane	5	12
tetrahydrofuran	6	2
toluene	7	1
dichloromethane	8	3
acetic acid	9	11
acetonitrile	10	14
Average solvents used	**75 kg/kg API**	**94 kg/ kg API**

Green Chem. **2011**, *13*, 854-862

溶劑之回收與處理

- Chemical treatment technologies for **waste-water** recycling—an overview (*RCS Adv*. **2012**, *2*, 6380-6388)
- STEP wastewater treatment: A solar thermal electrochemical process for pollutant oxidation (*ChemSusChem* **2012**, *5*, 2000-2010)
- The importance of **acetonitrile** in the pharmaceutical industry and opportunities for its recovery from waste (*Org. Process Res. Dev*. **2012**, *16*, 612-624)
- Green design alternatives for **isopropanol** recovery in the celecoxib process (*Clean Techn. Environ. Policy* **2012**, *14*, 697-698)
- Pervaporation as a green drying process for **tetrhydrofuran** recovery in pharmaceutical synthesis (*Green Chem. Lett. Rev*. **2012**, *5*, 55-64)

Replacement of dichloromethane

- A convenient guide to help select replacement solvents for dichloromethane in chromatography

  Green Chem. **2012**, DOI: 10.1039/C2GC36064K

- Replacement of dichloromethane within chromatographic purification: a guide to alternative solvents

  Green Chem. **2012**, DOI: 10.1039/C2GC36378J

- 2-Methyltetrahydrofuran (**2-MeTHF**) is a good substitute for CH_2Cl_2

  A general review on 2-MeTHF, *ChemSusChem*, **2012**, *5*, 1369-1379

Alternative solvents (Neoteric solvents)

- Water
- Supercritical and near-(or sub-)critical fluid systems
- Other benign solvents (ionic liquids, gas-expansion liquids, etc.)
- Polymeric solvents and less-volatile solvents
- Renewables (bio-derived, *e.g.*, glycerol derivatives）
- [Fluorous solvents]
- Switchable systems

Kerton, *Alternative Solvents for Green Chemistry*, RSC, 2009

Alternative solvents

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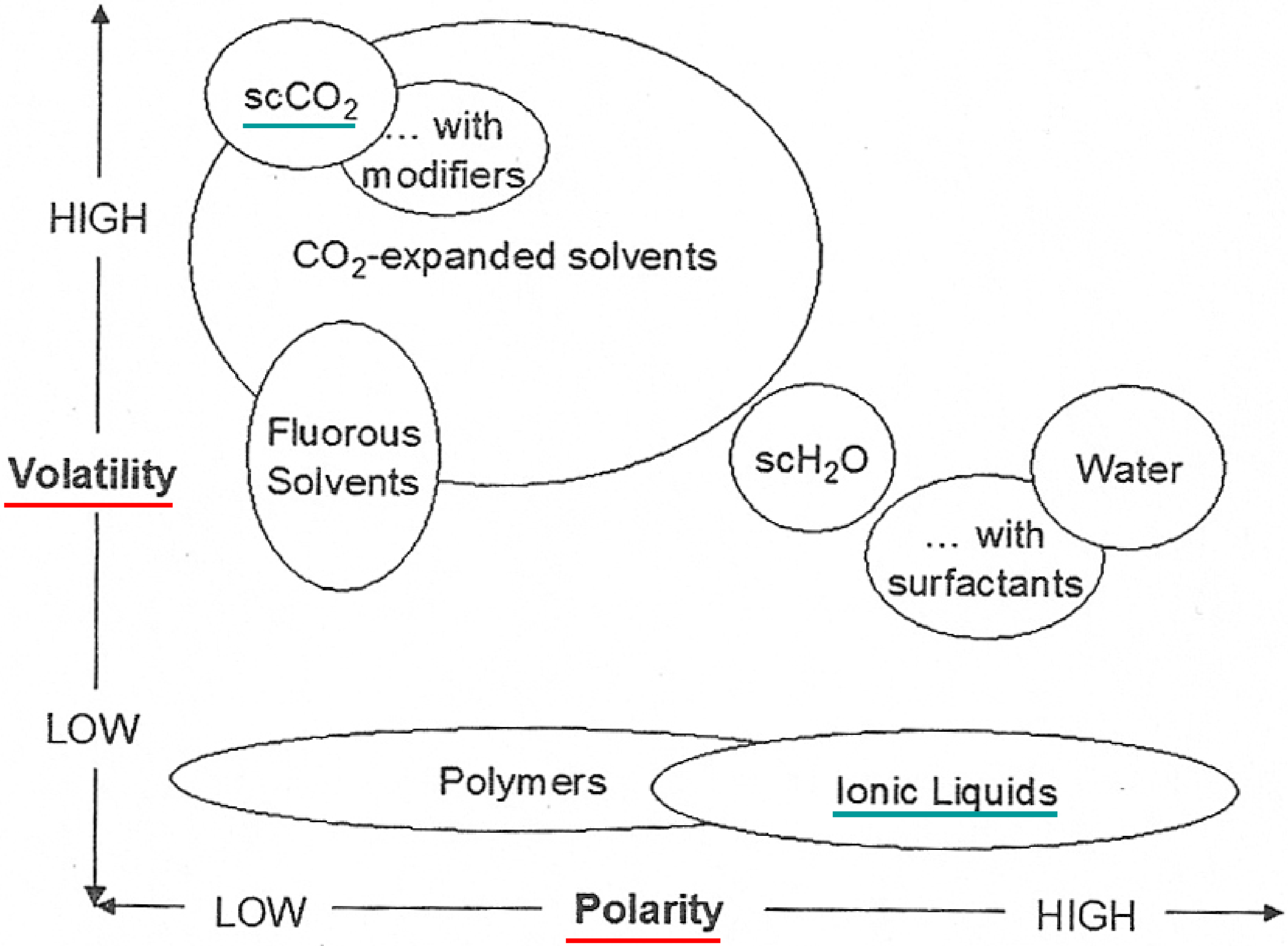
Polarity and volatility characteristics



(Kerton, *Alternative Solvents for Green Chemistry*, RSC, **2009**, p. 17)

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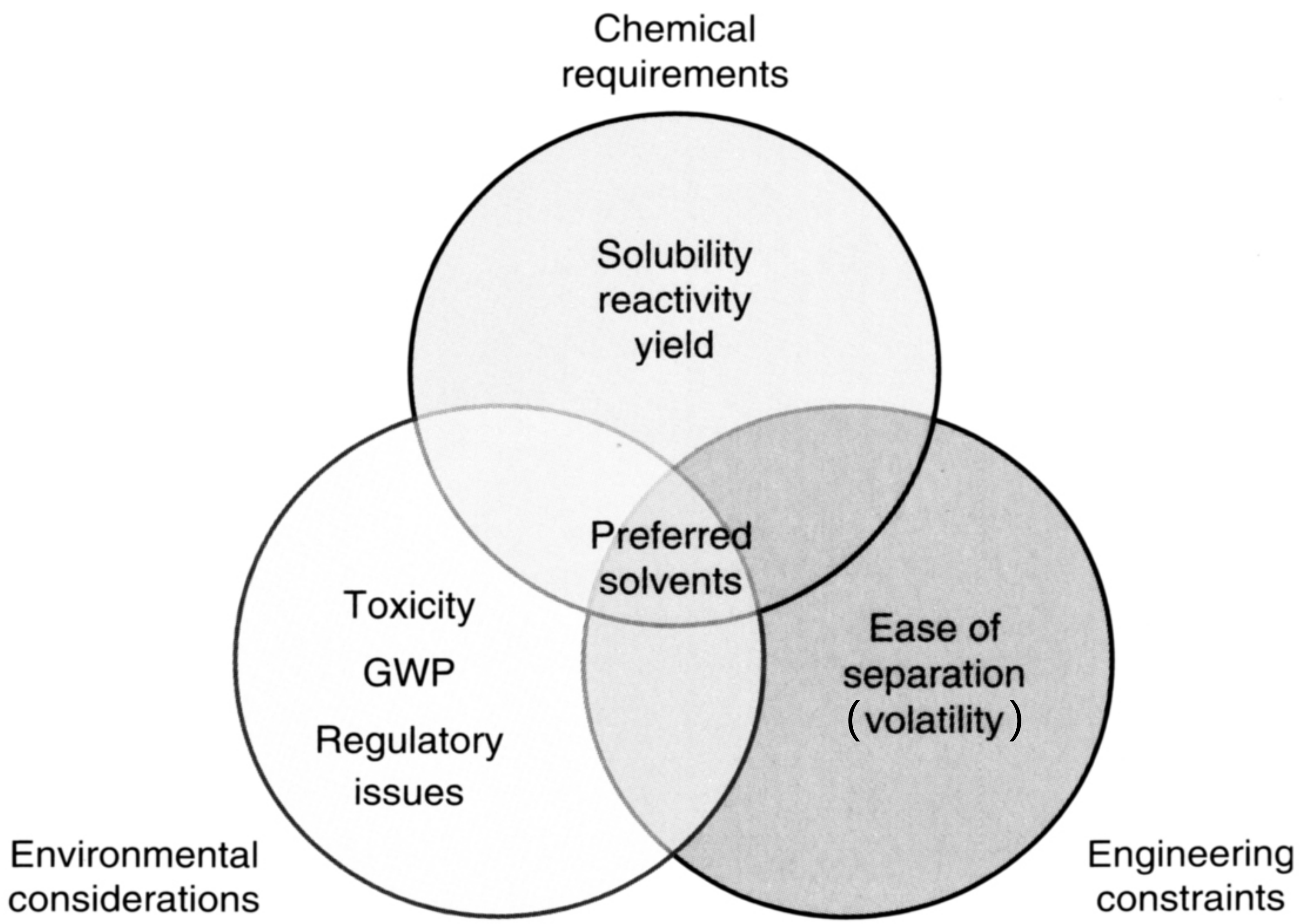
Conceptual basis for preferable solvent selection



Green Chemistry Metrics, p.22 (Blackwell, **2008**)

Supercritical fluids and critical points

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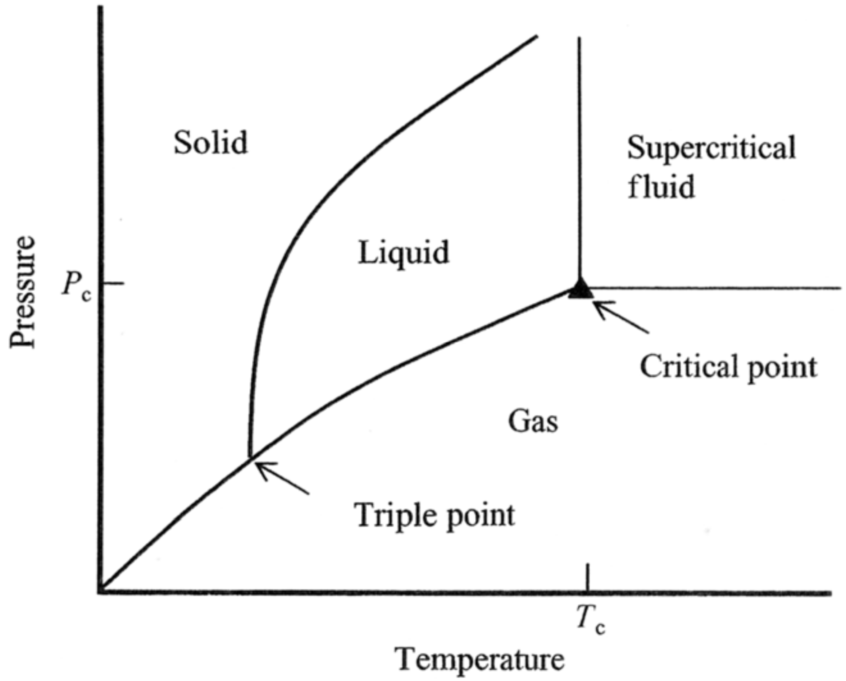

Material	T_c (°C)	P_c (bar)
Ammonia	132.4	113.2
Carbon dioxide	31.1	73.8
Ethane	32.2	48.7
Ethene	9.2	50.4
Fluoroform	25.9	48.2
Propane	96.7	42.5
Water	374.2	220.5

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Water

Subcritical Water as Reaction Environment
ChemSusChem, **2011**, *4*, 566-579.

Green material synthesis with supercritical water
Green Chem. **2011**, *13* 1380-1390.

Near-critical water for synthesis of metal-organic framework *Chem. Soc. Rev.* **2012**, *41*, 117-122.

Green chemistry oriented org. synthesis in water
Chem. Soc. Rev. **2012**, *41*, 1515-1527

Aqueous biphasic system: a boost brought about by using ionic liquids

Chem. Soc. Rev. **2012**, *41*, 4966-4995

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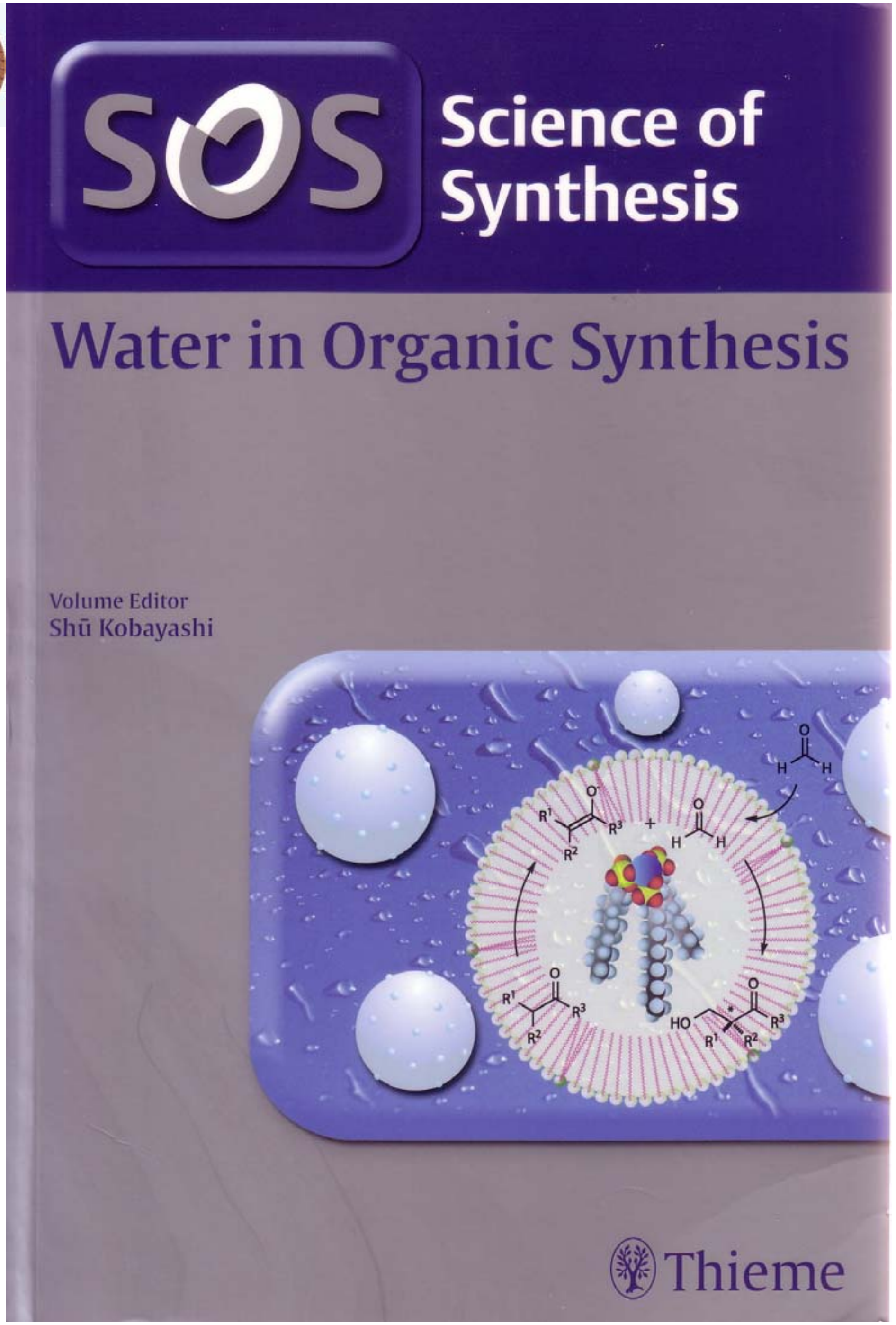

Ed. S. Kobayashi, **2012**

1. Introduction
2. Structure and Properties
3. Reactions of C-C multiple bonds
4. Reactions of C=O and C=N
5. Cyclization, Rearrangement, etc.
6. Special techniques in water
7. Industrial applications
8. Perspective

(＞1000 pages)

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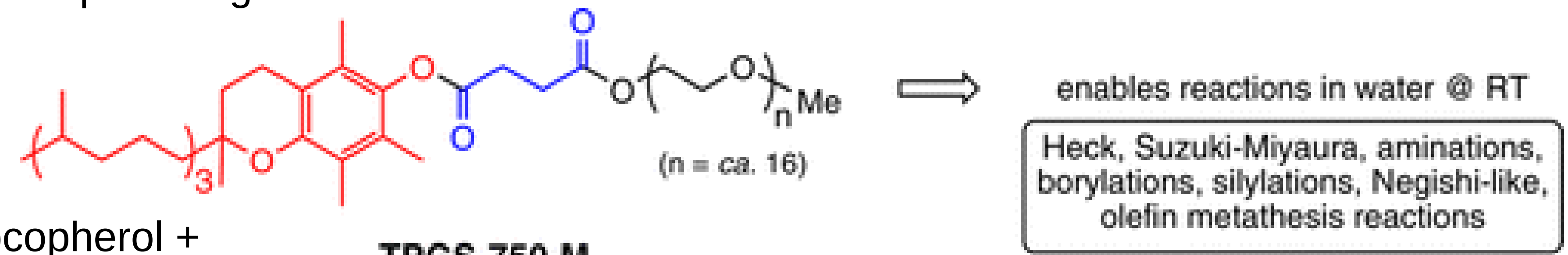
Surfactant for aqueous-organic reactions

PGCC Academic Award 2011

Professor Bruce H. Lipshutz, Department of Chemistry and Biochemistry, University of California, Santa Barbara

Innovation and Benefits

Most chemical manufacturing processes rely on organic solvents, which tend to be volatile, toxic, and flammable. Chemical manufacturers use billions of pounds of organic solvents each year, much of which becomes waste. Water itself cannot replace organic solvents as the medium for chemical reactions because many chemicals do not dissolve and do not react in water. Professor Lipshutz has designed a safe surfactant, **TPGS-750-M,** that forms tiny droplets in water. Organic chemicals dissolve in these droplets and react efficiently, allowing water to replace organic solvents.



α-tocopherol +

TPGS-750-M

$(CH_2CO)_2O$, then PEG-750-M

(*J. Org. Chem.*, **2011**, *76*, 4379-4391.)

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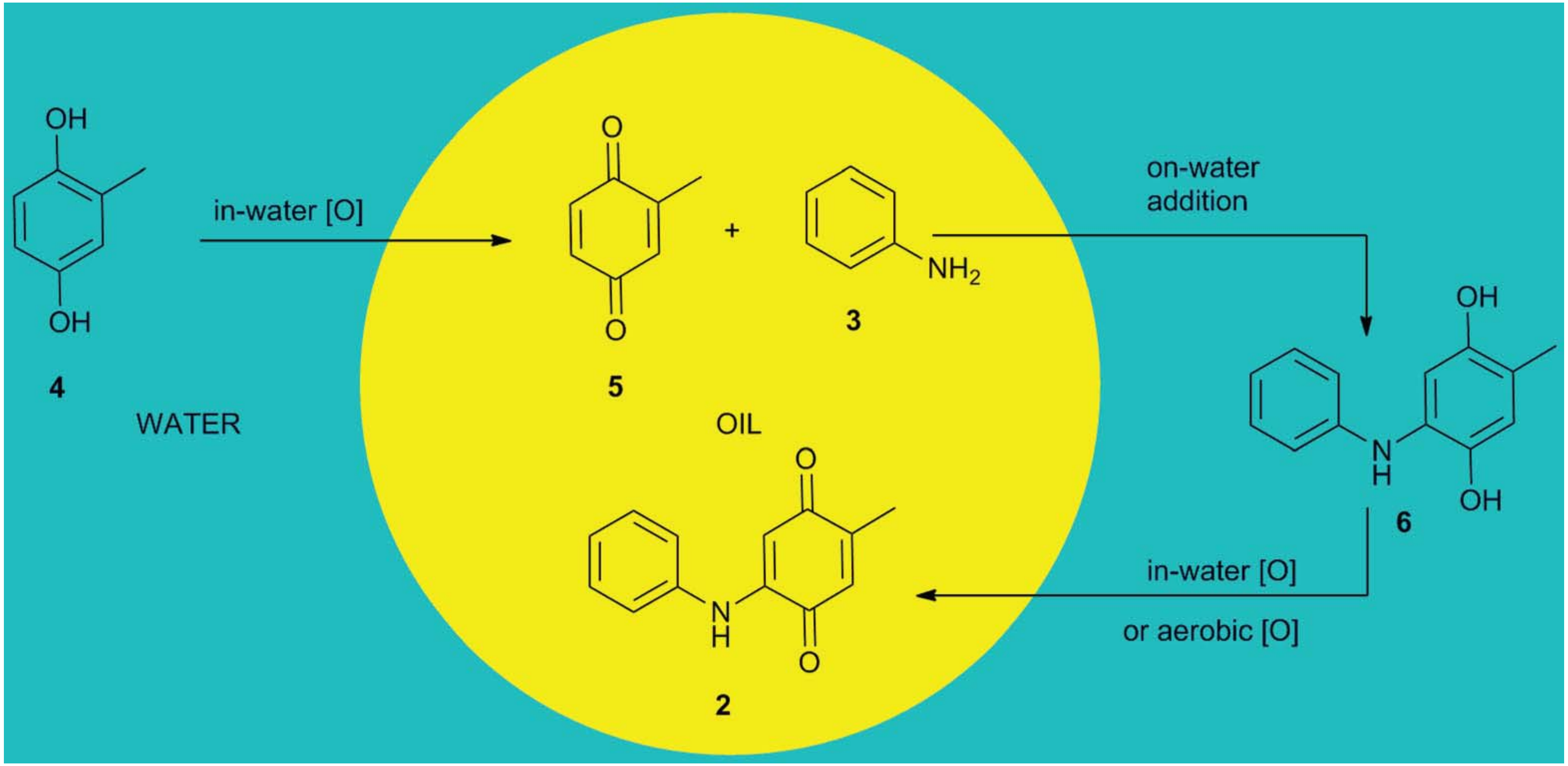
In-water, on-water domino process

(*Chem. Eur. J.* **2010**, *16*, 8972-8974; *Green Chem*. **2012**, *14*, 605-609)



Hydrophobic Effects

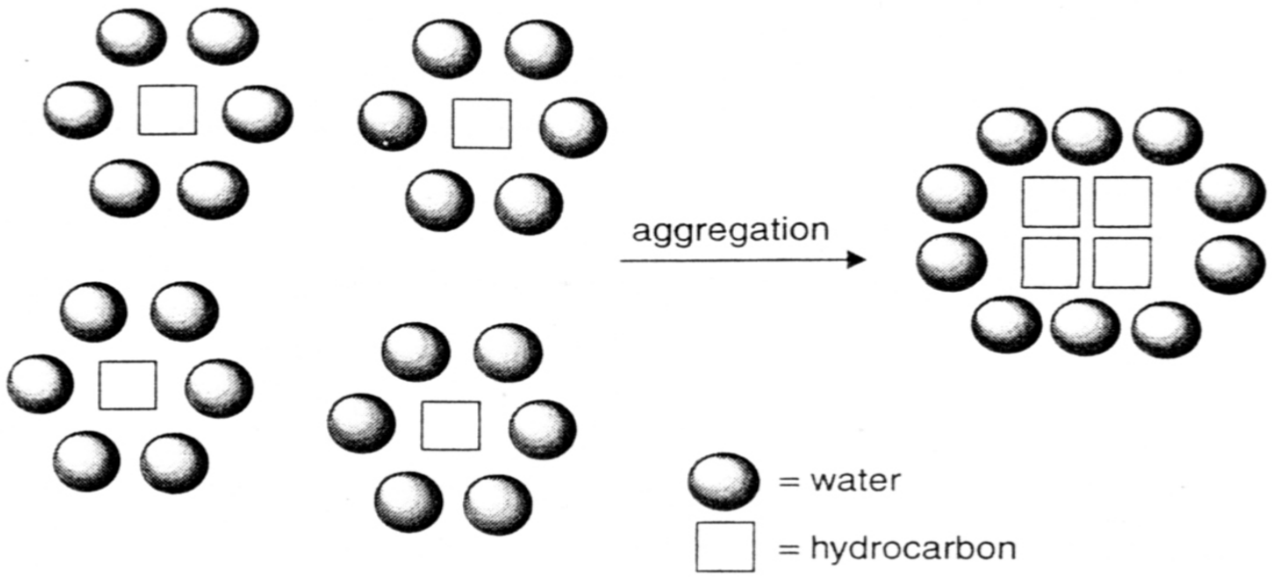
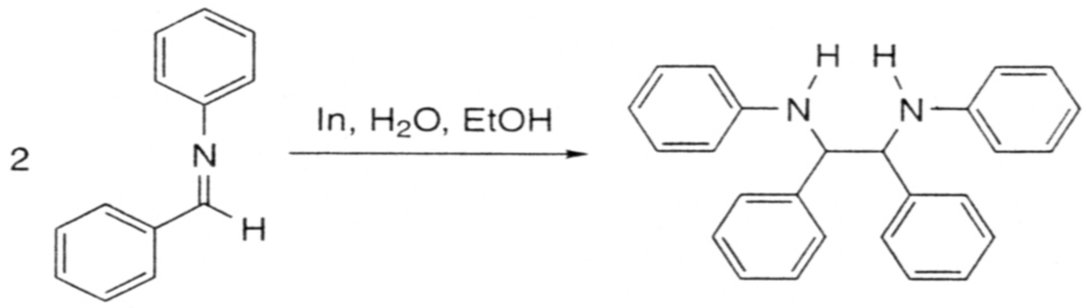


Figure 5.5 The hydrophobic effect. Aggregation of hydrocarbon molecules in water reduces the number of molecules with restricted motion



Scheme 5.1 Indium mediated imine coupling

Adams, *et al*., *Chemistry in Alternative Reaction Media*, **2004** , Wiley, p. 101

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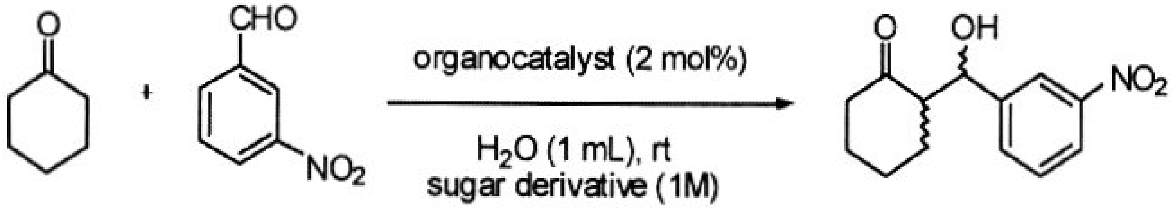
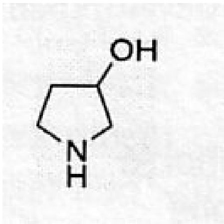
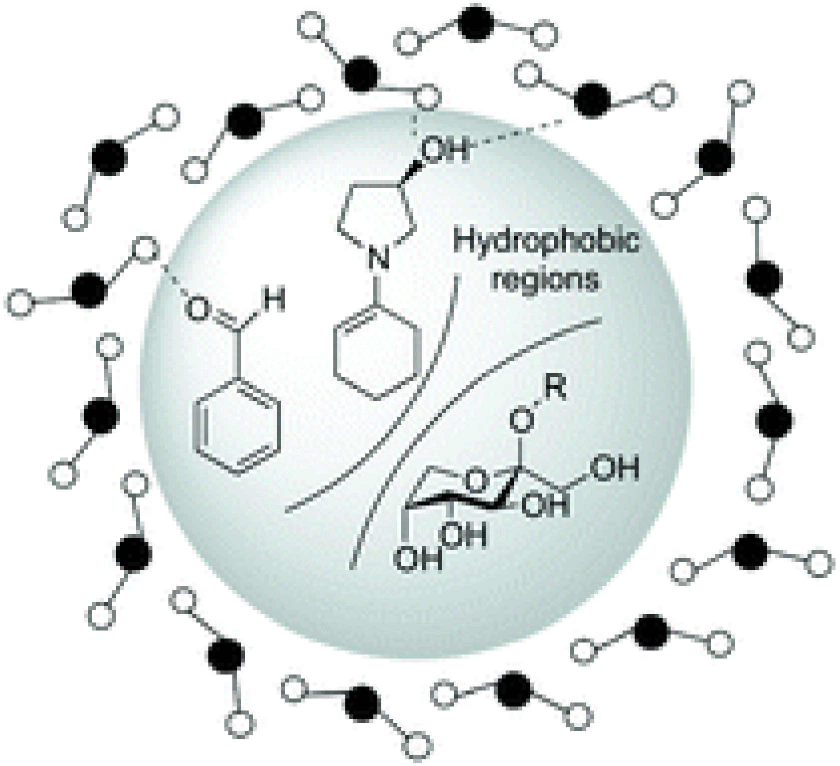
Organocatalyzed direct aldol reactions were efficiently performed in aqueous solutions of facial amphiphilic carbohydrates with high diastereoselectivity and yields.

（***Green Chem.***, 2012, **14**, 281-284 ）



Catalysts, *e.g.*





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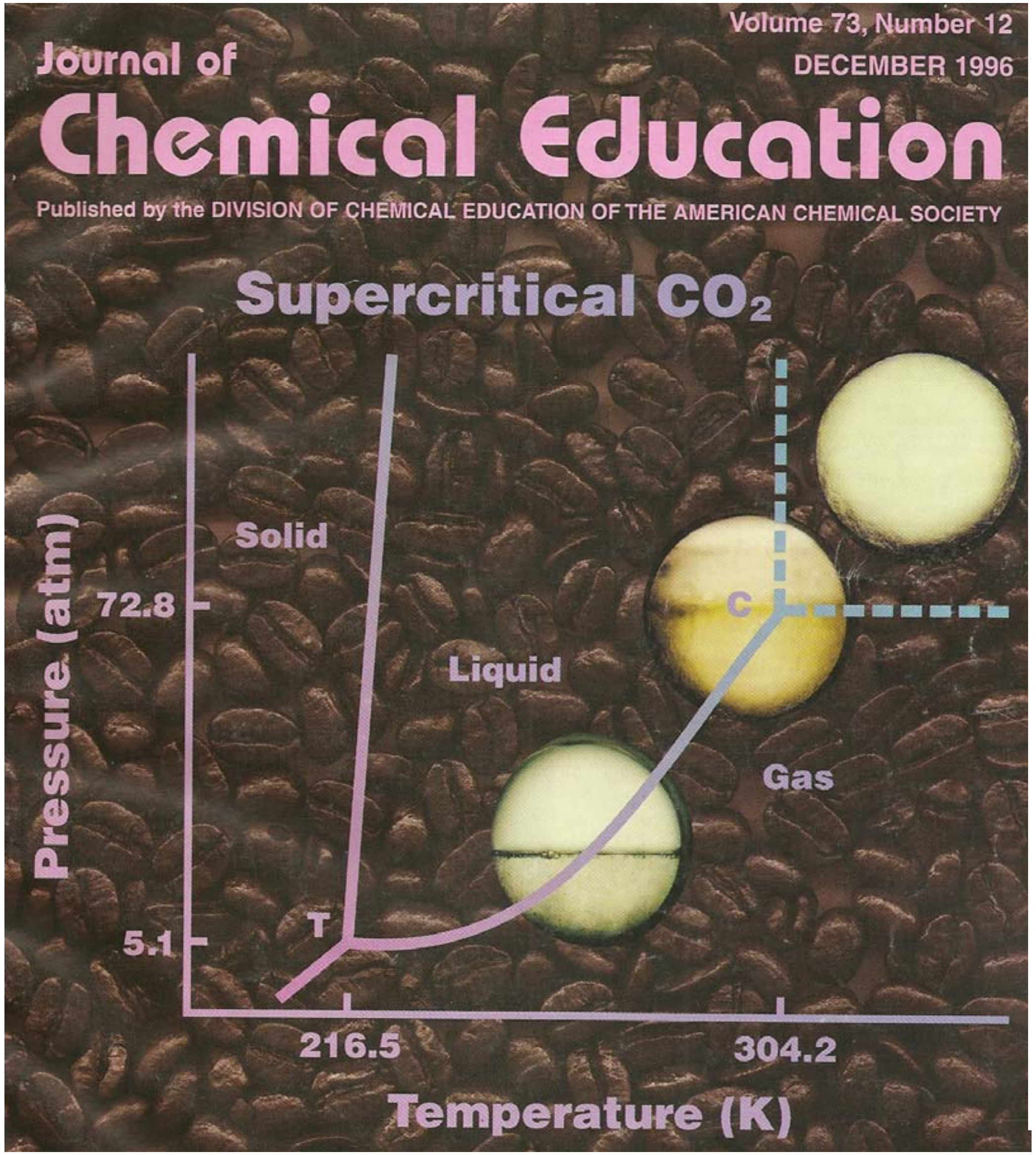
$ScCO_2$ “老” 技術



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

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

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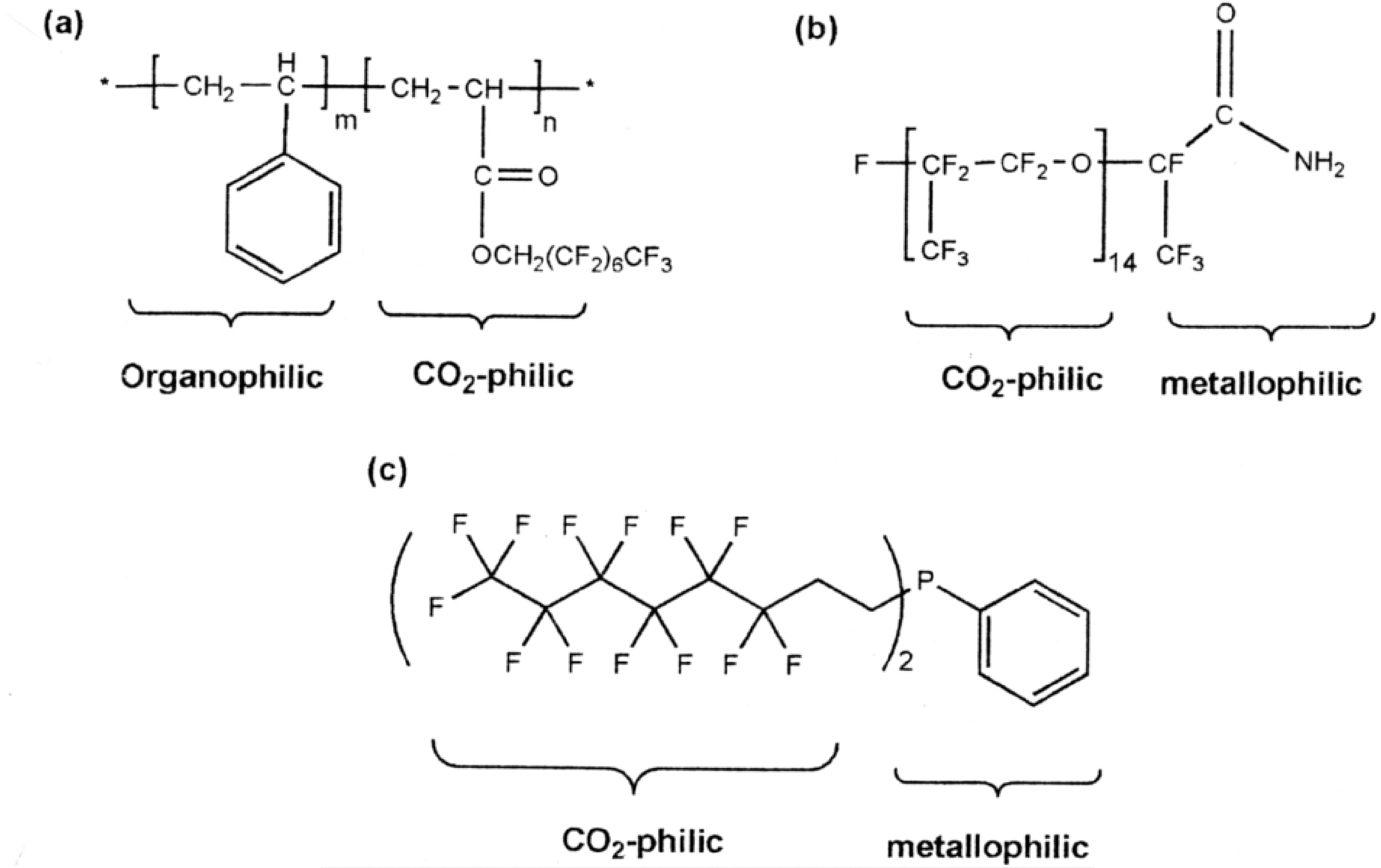
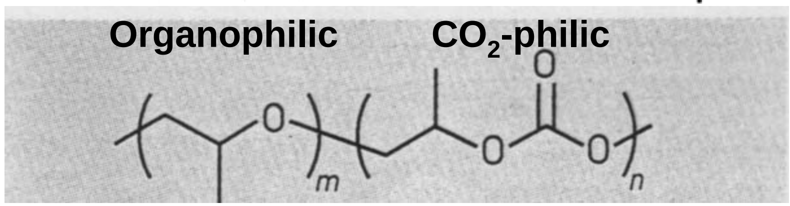
New Surfactant for Sc-CO_2





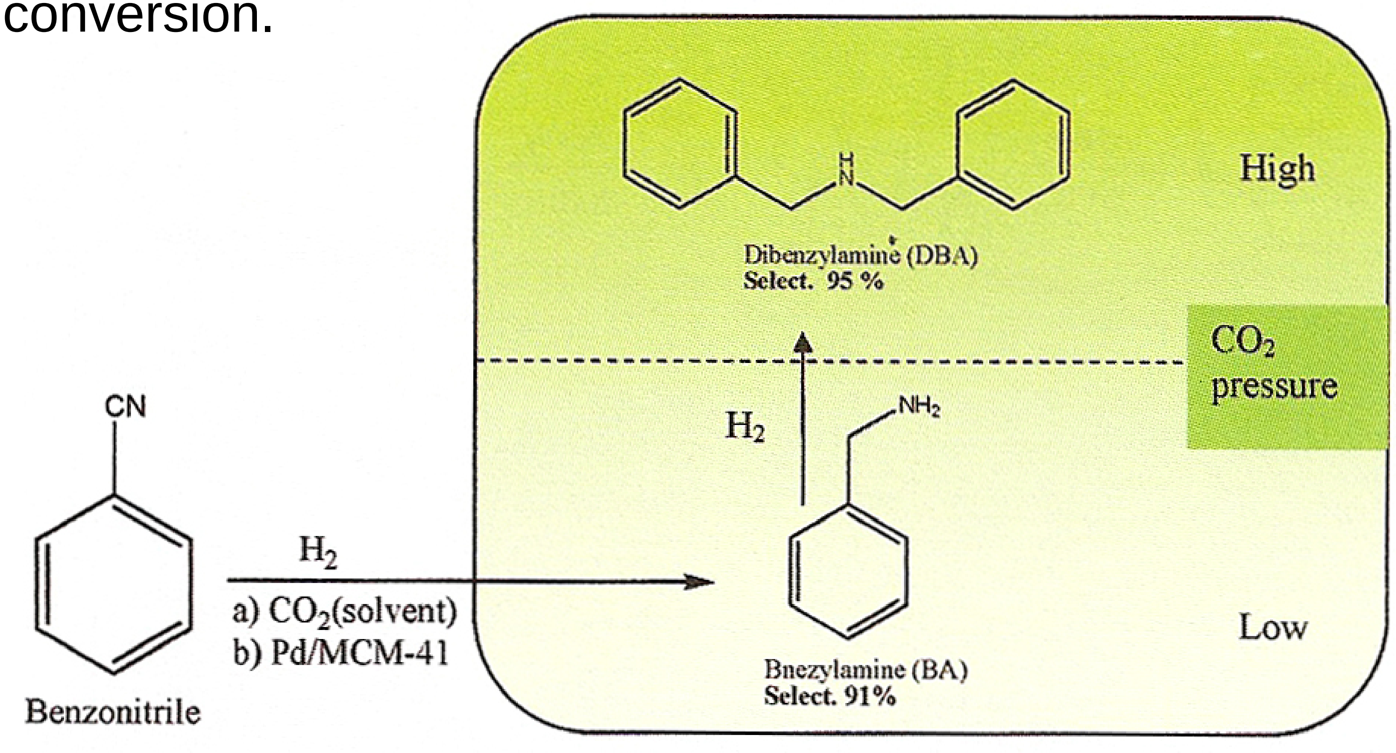
Non-fluorinated (ether-carbonate) copolymer by Beckman and coworkers at U. of Pittsburgh. **PGCC Award of 2002**

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

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

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.



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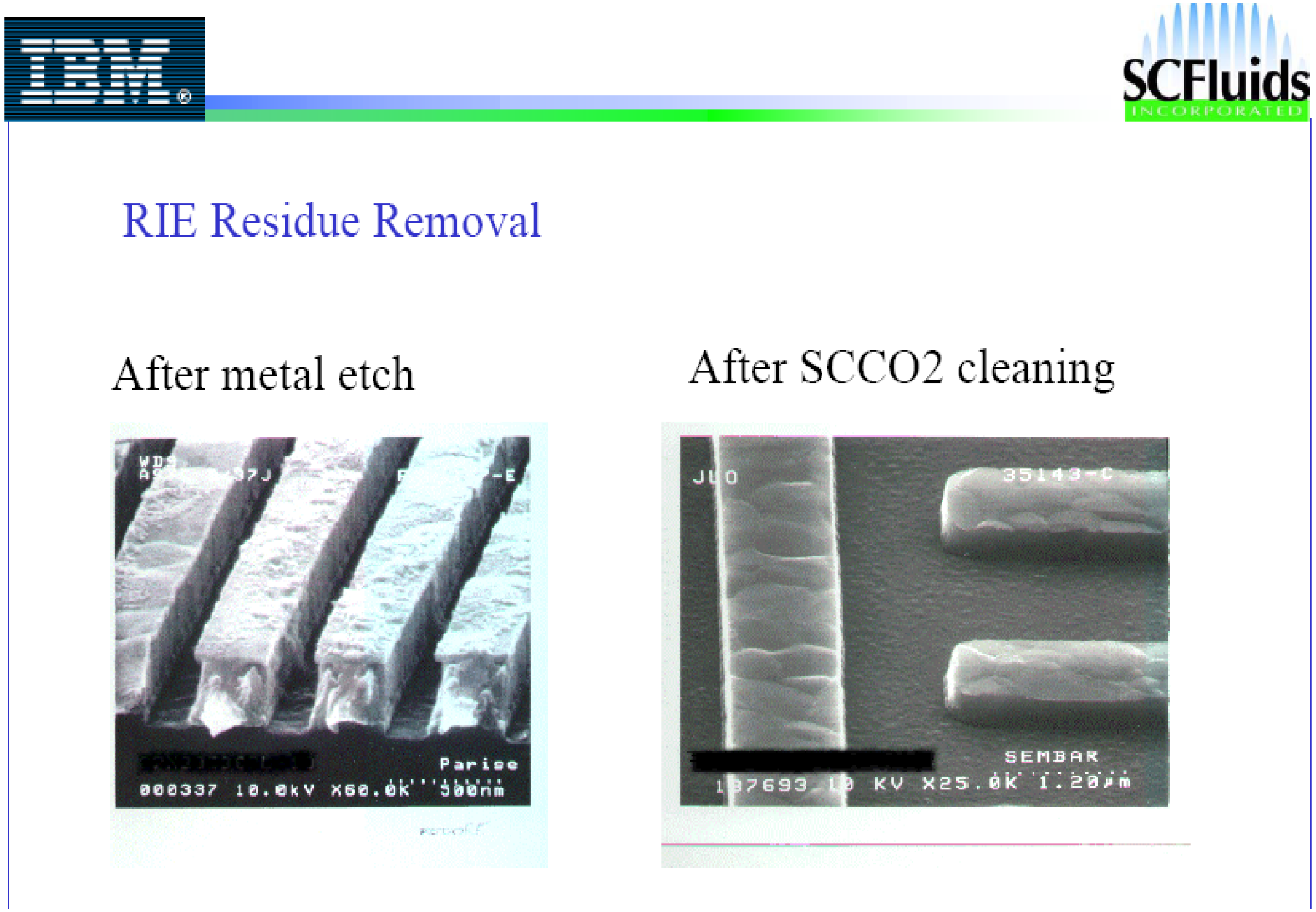
Industrial applications

- **Extraction of fatty and resin acids from dried pine dust with $scCO_2$ to reduce auto-oxidation** (*RCS Adv*. **2012**, *2*, 1806-1809)
- 

Room temperature ionic liquids

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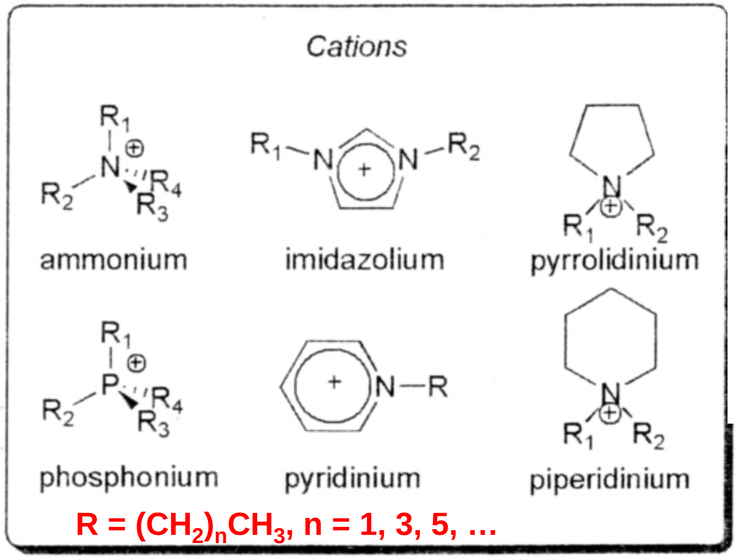


Anions

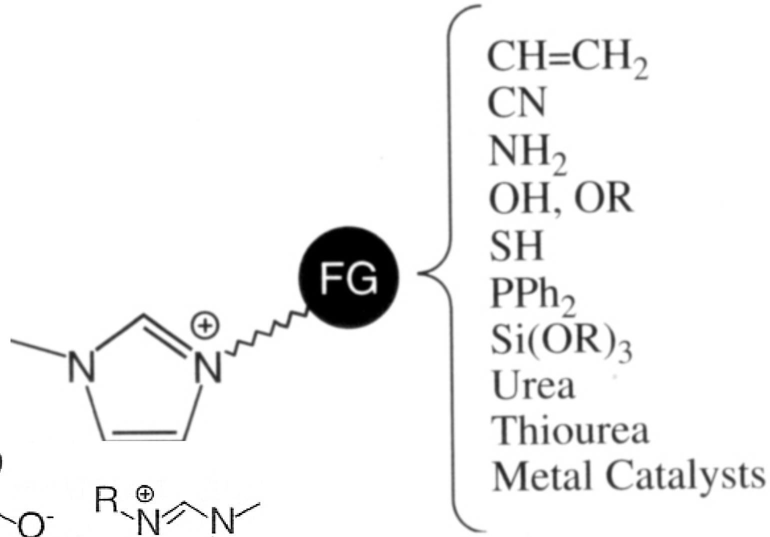
NO_3^-	BF_4^-	$CF_3SO_3^-$	Cl^-, Br^-, I^-
$Al_2Cl_7^-$	SbF_6^-	$CF_3CO_2^-$	$CH_3CO_2^-$
$Me_2PO_4^-$	PF_6^-	$(CF_3SO_2)_2N^-$	$(CN)_2N^-$

(**RTIL**)

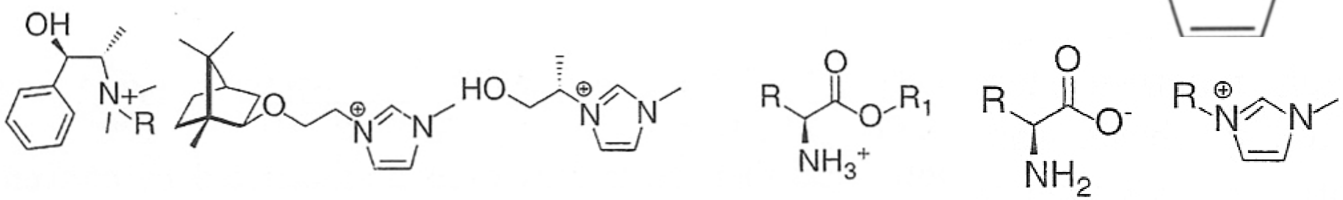
Alternative Solvents for Green Chemistry (Kerton, **2009, RSC**)Chapter 5

Task-specific ionic liquids (TSIL)

Functionalized ionic liquid cations



Novel chiral ionic liquids



Ballini (Ed), *Eco-Friendly Synthesis of Fine Chemicals*, Chapter 4, RSC, **2009**)

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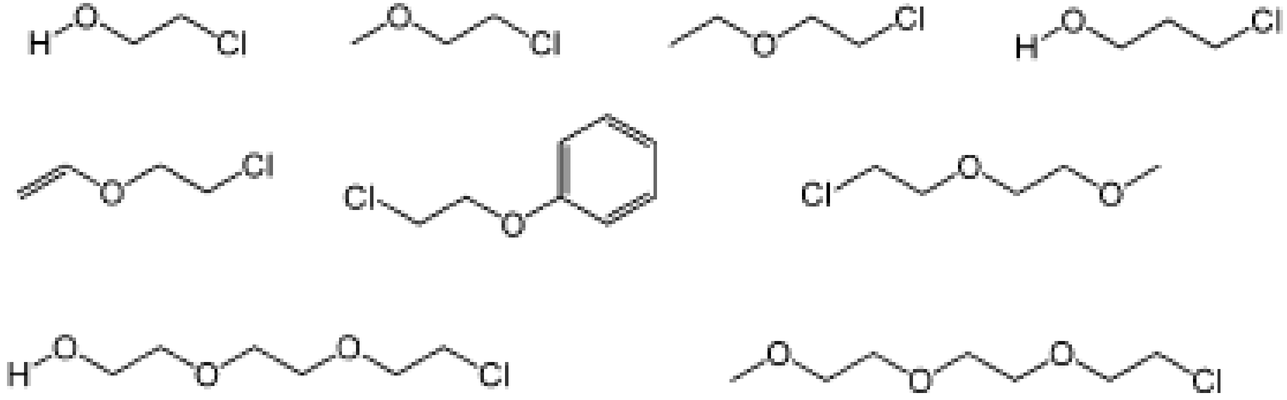
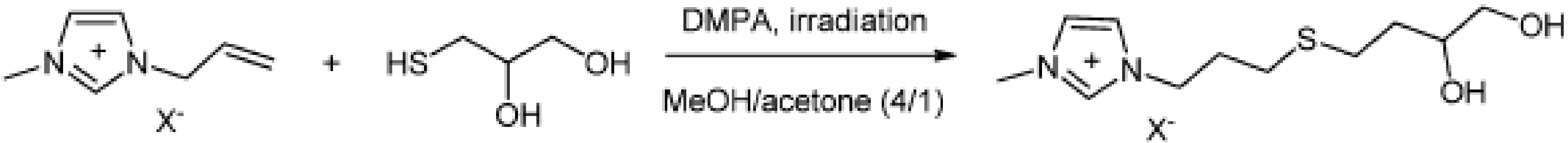
Ether- and alcohol-functionalized task-specific ionic liquids

New ether- and alcohol-functionalized ionic liquids have gained tremendous attention in various applications due to their attractive physicochemical properties.

R_2Cl could be one of these chlorides (sometimes bromides):





X = Cl, Br, or Tf_2N

Chem. Soc. Rev., 2012, **41**, 4030-4066

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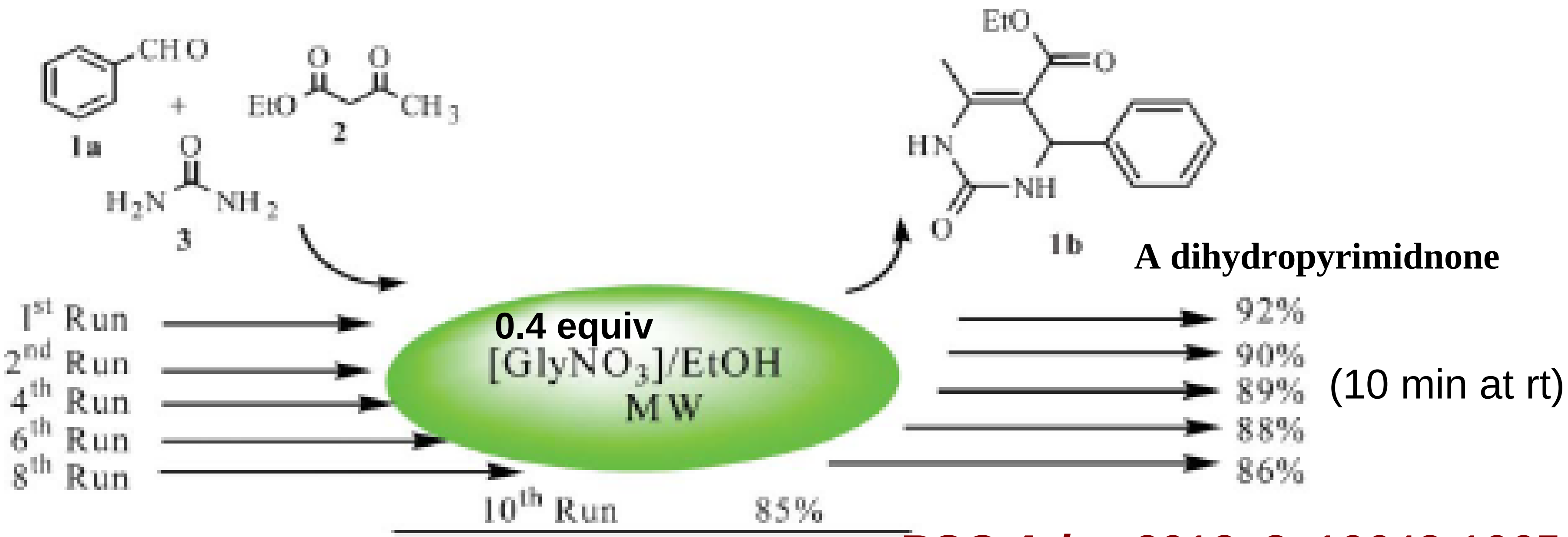
Glycine nitrate, an inexpensive, recyclable and biodegradable ionic liquid

Microwave assisted 3-component Biginelli reaction



RSC Adv., 2012, **2**, 10648-10651

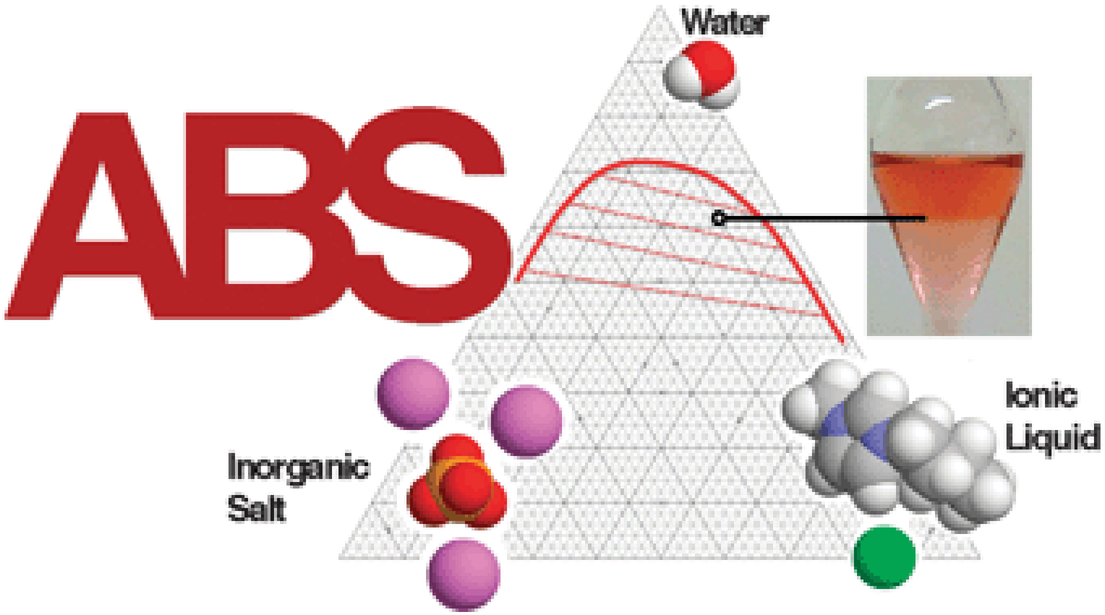
Biodegradation studies of ionic liquids

Neumann, *et al. Green Chem*, **2012**, *14*, 410-418
Trivedi, *et al*. *ChemSusChem* **2011**, *4*, 604-608
Coleman and Gathergood, *Chem. Soc. Rev.*, **2010**, *39*, 600 - 637
Harjani, *et al*. *Green Chem.*, **2010**, *12*, 650 – 655

Aqueous Biphasic System

Chem. Soc. Rev. **2012**, *41*, 4966-4995

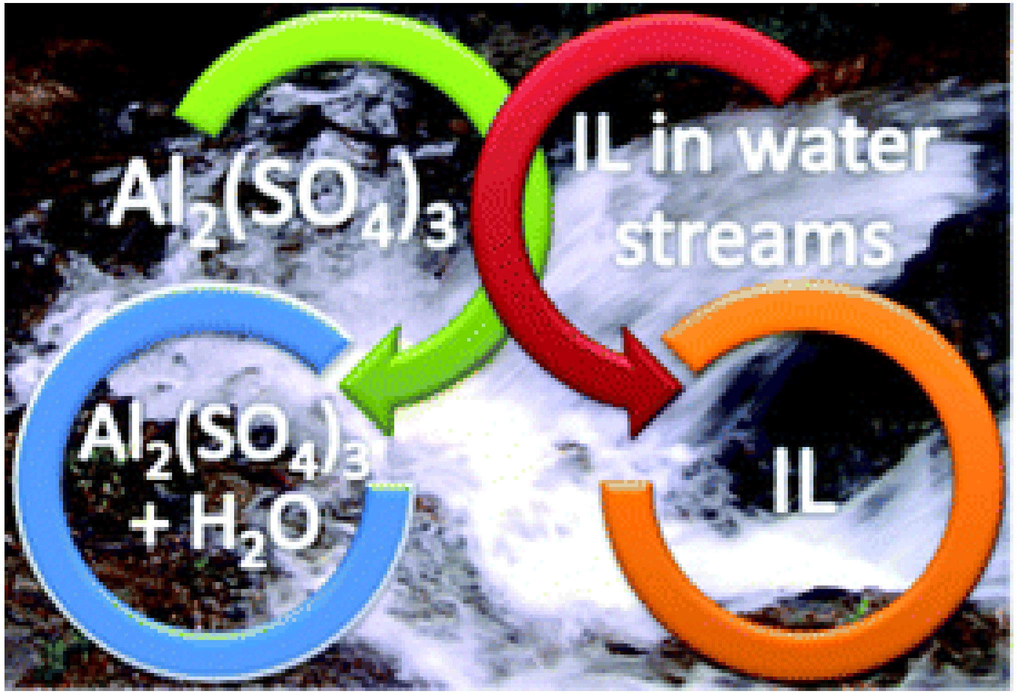
This *critical review* provides a judicious assessment of the literature and highlights future challenges to the field of ionic-liquid-based ABS.



Extraction of Puerarin using ABS

Sep. Sci. Techn. **2012**, *47*, 1740-1747

A novel technique using aluminium-based salts allows **96-100% recovery of ionic liquids** containing imidazolium-, pyridinium- and phosphornium-based fluids from aqueous streams

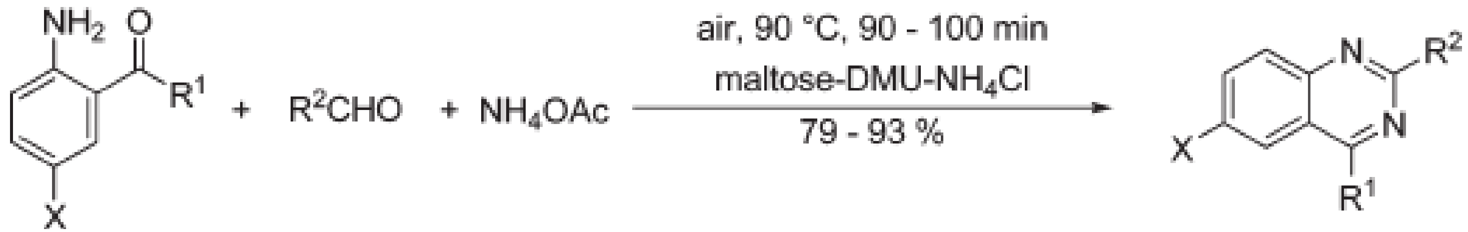


RSC Adv. **2012**, **DOI:** 10.1039/C2RA21535G

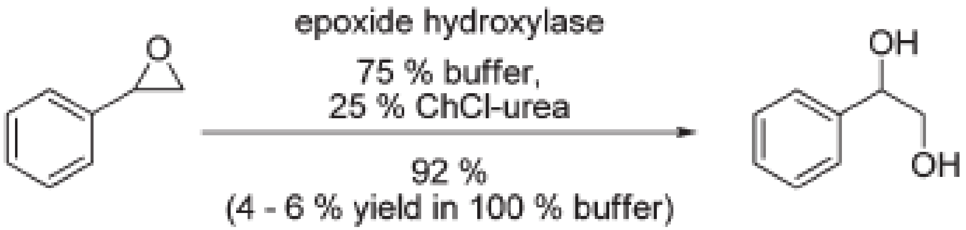
An alternative to ionic liquids

Natural compounds have recently been used to produced deep eutectic solvents (choline chloride + RCOOH, or ROH, or urea), sugar melts (carbohydrate + urea or DMU + NH_4Cl or MCl), or ionic liquids.This review presents physicochemical data of these reaction media and highlights recent advances in their use in organic synthesis and bio-transformations.

Catalyst free quinazoline multicomponent synthesis[70]



Epoxide hydrolysis[33]



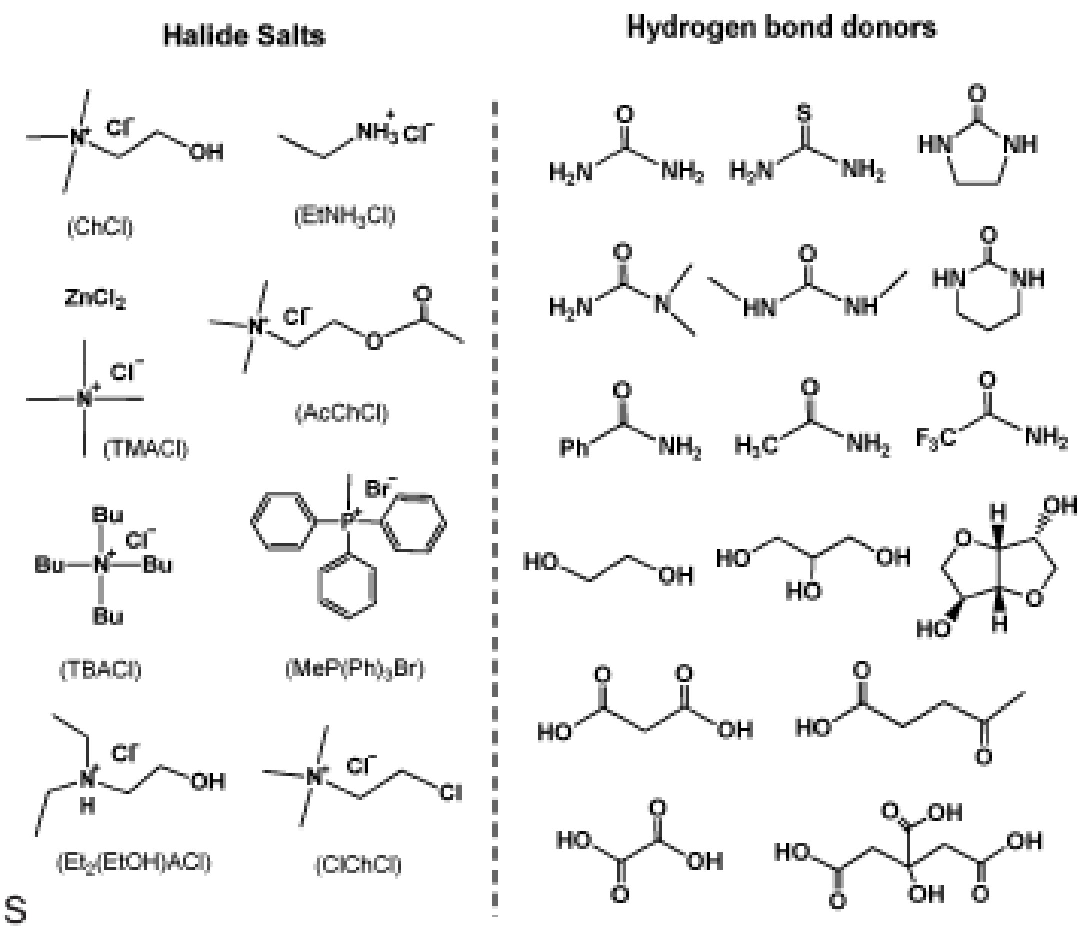
Carolin Ruß and Burkhard König

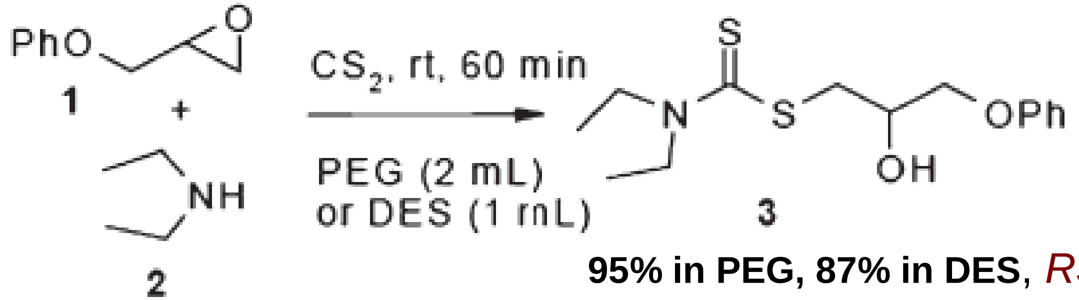
Green Chem. **2012**, DOI: 10.1039/c2gc39005e

Deep eutectic solvent

A type of ionic solvent with special properties of a mixture which forms a eutectic with a mp much lower than both individual components. e.g., mp for choline chloride is 302^{o}C urea is 133^{o}C, the (1:2) eutectic mixture is 12^{o}C.

Chem Soc. Rev. **2012**, *41*, 4996-5014; 7108-7146





95% in PEG, 87% in DES, *RSC Adv*, **2012**, *2, 7413-7416*

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Deep-eutectic Solvents

Synthetic processes based on the use of deep-eutectic solvents are useful to prepare a range of materials with tailored morphologies and compositions.

Chem. Soc. Rev. **2012**, *41*, 4996-5014

Deep Eutectic Solvents (DES) are an emerging new class of solvents that are highly attractive for the design of eco-efficient processes. **Advantages include biocompatible, low price, poorly toxic, biodegradable, easy to prepare and purify.**

Chem. Soc. Rev. **2012**, *41*, 7108-7146

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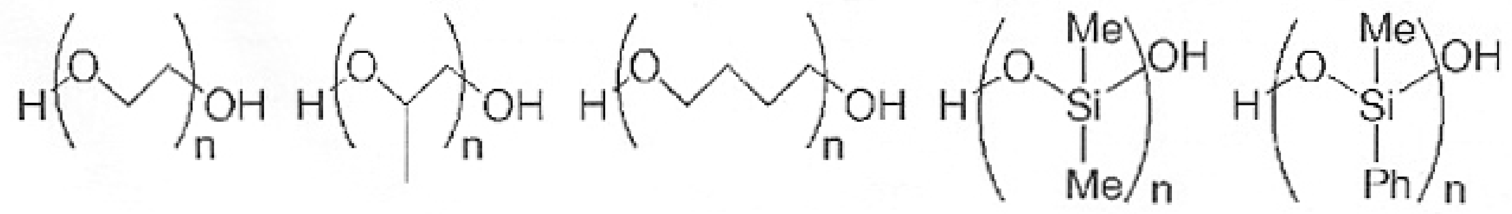
Liquid polymers as solvents



PEG	PPG	PTHF	PDMS	PMPS
poly(ethylene glycol)	poly(propylene glycol)	poly(tetrahydro-furan)	poly(dimethyl-siloxane)	poly(methyl-phenylsiloxane)

Table 1 Extent of biodegradation of polyethers by activated municipal sewage sludge after 14 days exposure[29]

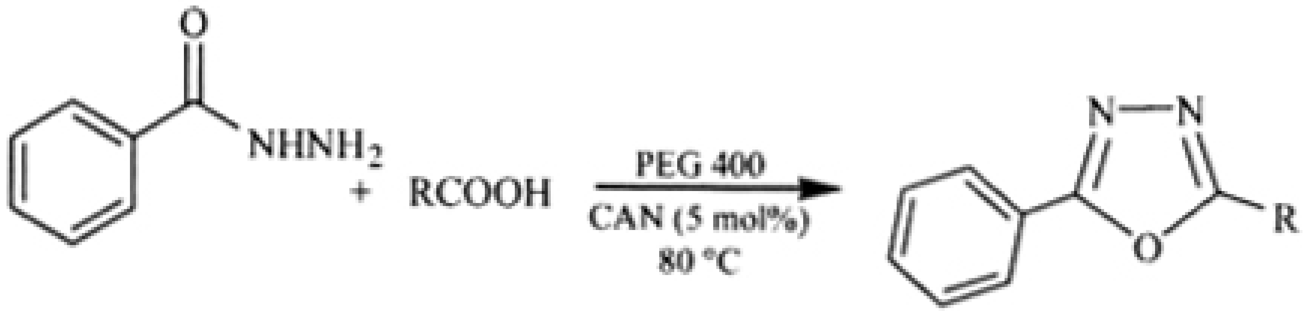
Polymer	M_n	Biodegradation (%)
PEG	390	99.7
PEG	1500	95.9
PEG-DME[a]	1500	9.4
PPG	410	69.7
PTHF	660	99.8

[a] PEG-dimethylether, $MeO(CH_2CH_2O)_nMe$

Green Chem. **2006**, *8*, 807-815

Synthesis of 2,5-disubstituted 1,3,4-oxadiazoles catalyzed by CAN in PEG

(*Green Chem. Lett. Rev*. **2010**, *3*, 55-59)

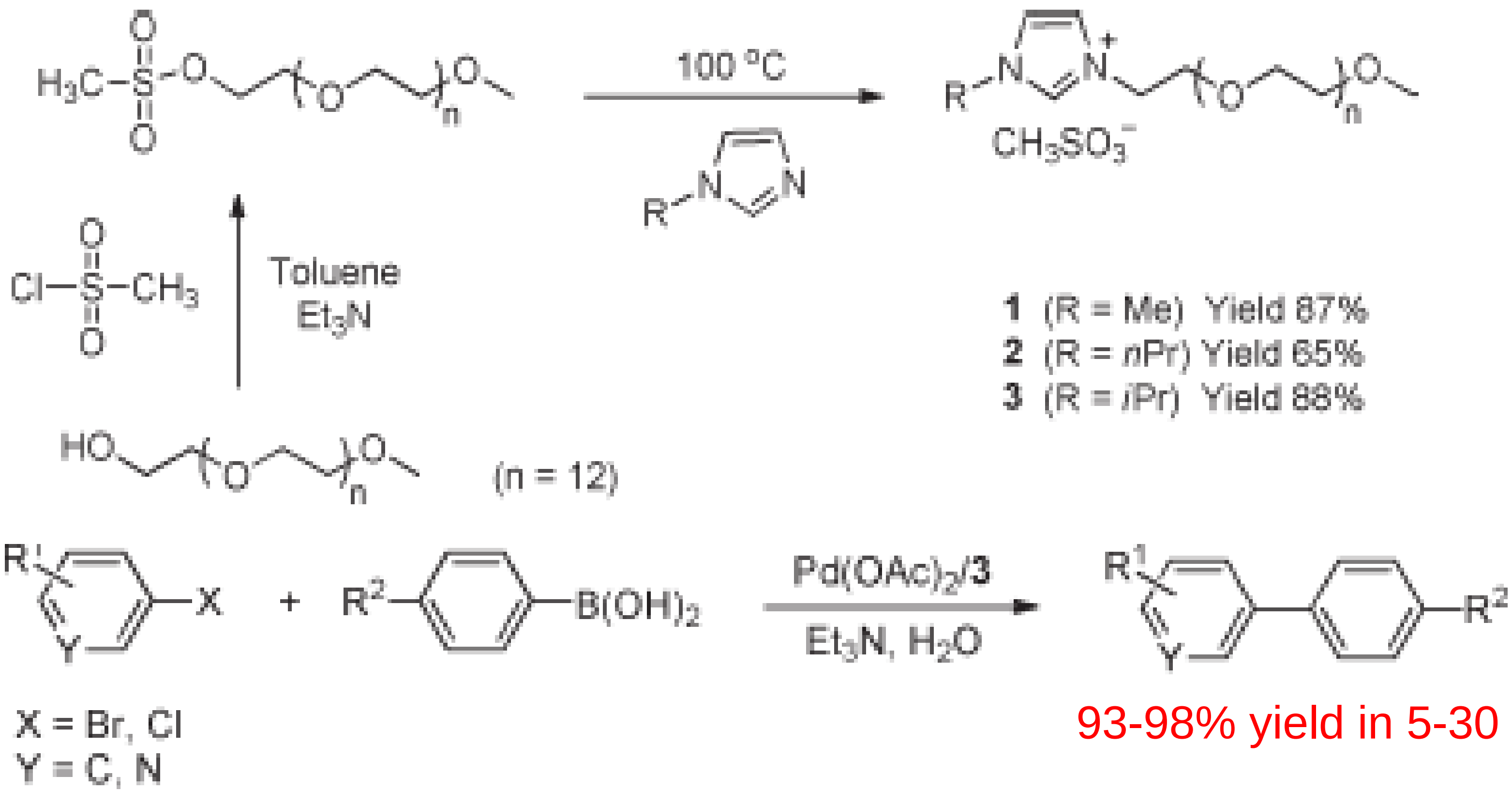


PEG was found the better solvent (faster and higher yield) than acetonitrile, ethanol and toluene. With 5 mole% of catalyst the reaction was done in 5 hr. The mixture was cooled in dry ice-acetone bath to precipitate PEG, and extracted with ether (PEG being insoluble). Isolation yield was 97-98%. The PEG (2% loss) could be reused for at least three times.

Newer applications, such as selective oxidation of sulfide to sulfoxide by PEG/O_2 (*Green Chem*. **2012**, *14*. 130-135)

PEG functionalized IL

Poly(ethylene glycol)-functionalized imidazolium salts–palladium-catalyzed Suzuki reaction in water.



93-98% yield in 5-30 min.

Green Chem. **2012**, *14*, 592-597

Solvents from renewable resources

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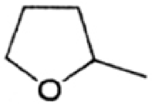
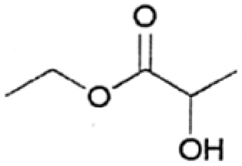
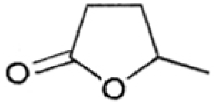


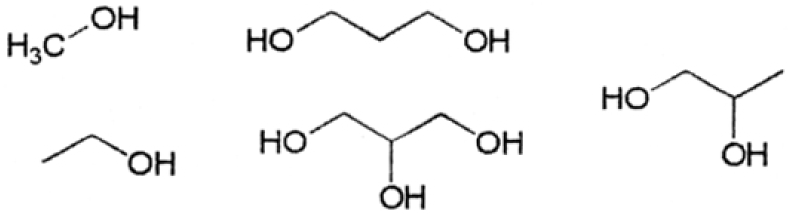
2-MeTHF
Bp 78



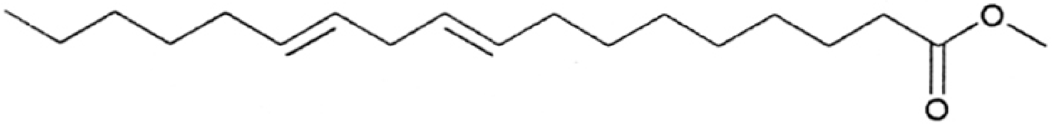
Ethyl lactate
151-155



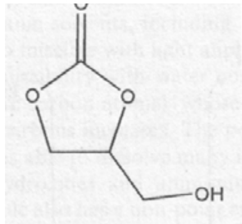
γ -Valerolactone
207-208 °C



Alcohols and polyols



Fatty acid ester (Biodiesel component)



Glycerol carbonate (and other organic Carbontes, R_2CO_3)

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

Some recent articles or reviews

γ-Valerolactone *Green Chem*. **2008,** *10* , 238-242

2-MeTHF: *ChemSusChem* **2012,** *5*, 1369-1379

Ethyl lactate: *Green Chem.* **2011,** *4*, 2658-2671

Glycerol: *Green Chem*. **2010**, *12*, 1127-1138

Ethylene glycol: *Chem. Soc. Rev.* **2012,** *41, 4218-4244*

Organic carbonates: *Chem. Rev*. **2010**, *110*, 4554-4581

Manufacturing Glycerol carbonate: *Org. Process. Res. Dev.* ***2012,*** *16, 389-399*

Organic carbonates as solvents

Table 1. Transport and Thermodynamic Properties

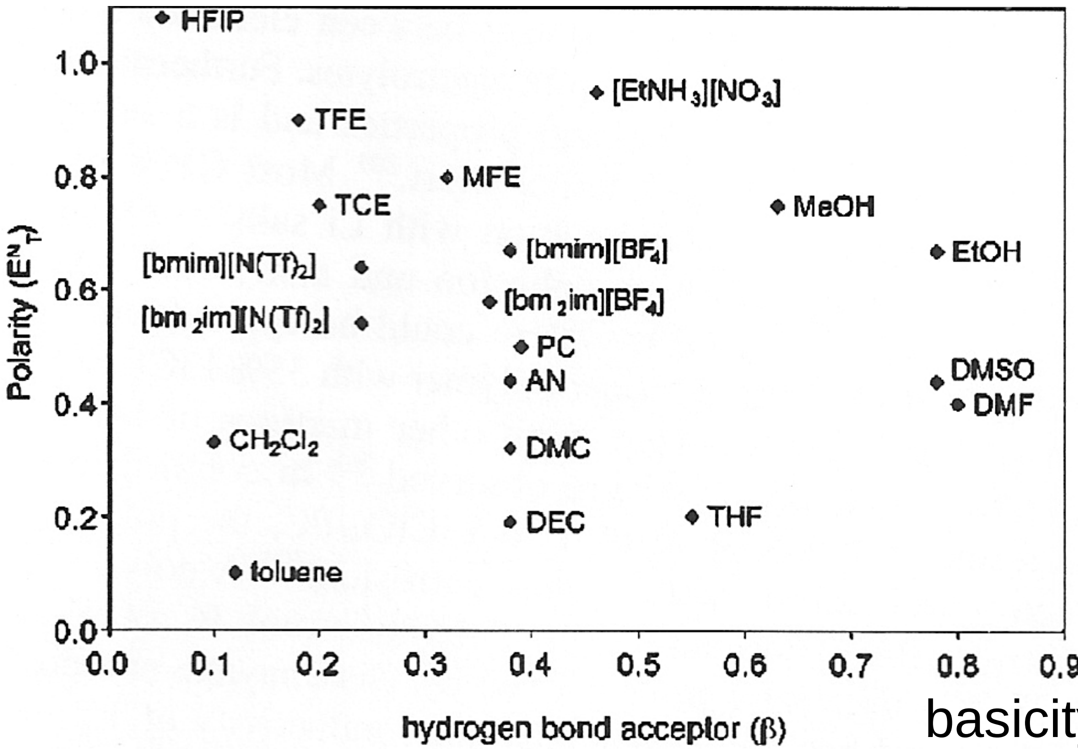
organic carbonate	bp [K]	d (293 K) [g/cm^3]	viscosity (298 K) [cP]
DMC	363[b]	1.07[b]	0.590[b]
DEC	399[b]	0.98[b]	0.753[c]
EC	521[d]	1.34[a,d]	2.56[a,d]
PC	515[d]	1.20[d]	2.50[d]
BC	524[d]	1.14[d]	3.14[c]

Acetone 0.320 cP

Water 0.891 cP

1-butanol 2.99 cP

polarity

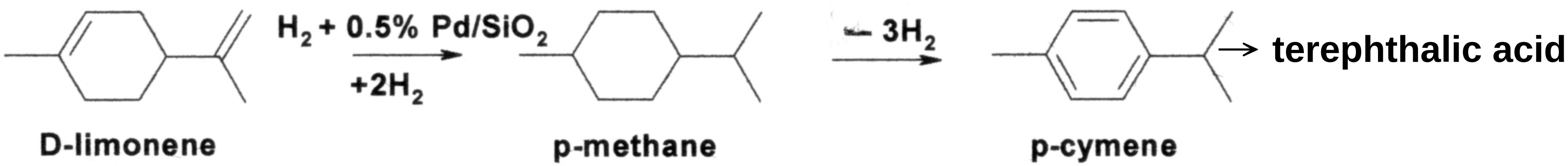


basicity

Inexpensive terpenes to useful chemicals

Limonene is a by-product of juice industry (50000 tpa in us). It can be used as non-toxic replacement in some medical applications.

It can be dehydrogenated to yield *p*-cymene, and then toTPA.



A solvent and an intermediate

Recently, Limonene was found to be used directly as solvent for certain reactions such esterification and amidation.

(*Green Chem*. **2012**, *14*, 90-93)

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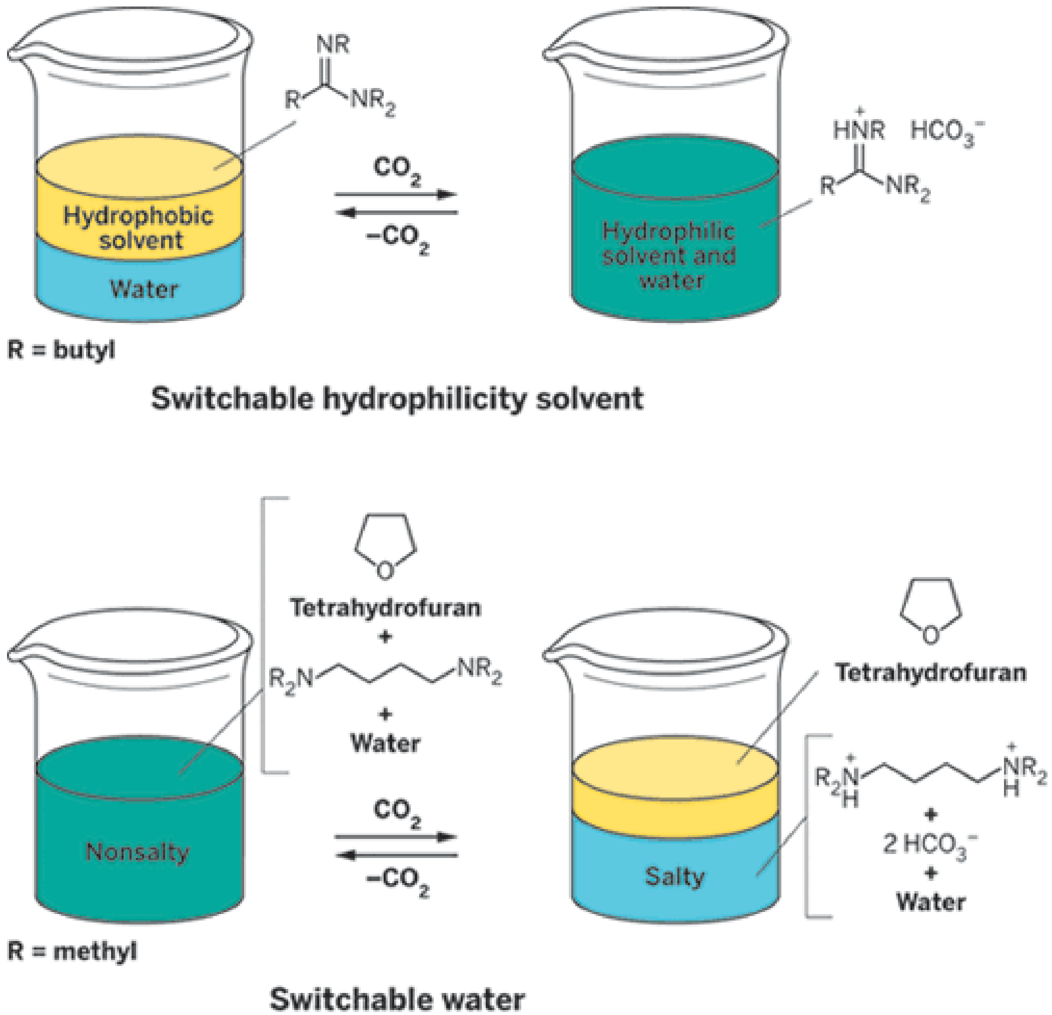
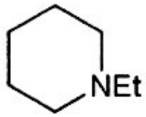
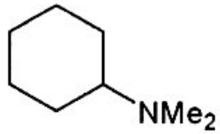
Switchable Water: Aqueous Solutions of Switchable Ionic Strength

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

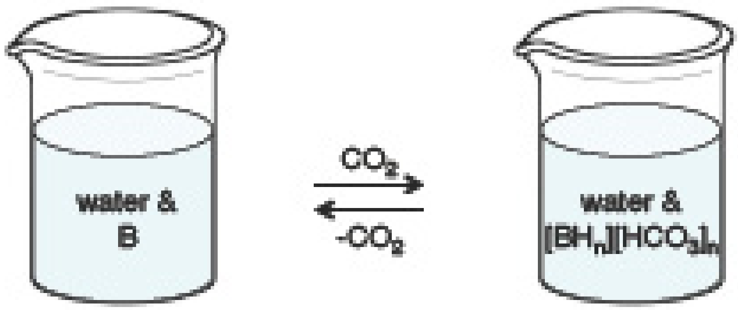


Tertiary amine and polyamines having switchable hydrophilicity

Jessop, *et al. Green Chem.* **2011**, *13*, 619-623; **2012,** *14,* 832-839

NEt_3	Me_2NBu	Et_2NBu	Pr_2NMe			$Me_2NC_6H_{13}$	
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
1.2	1.6	1.7	1.9	1.7	2.1	2.5	2.4

SWITCHABLE WATER

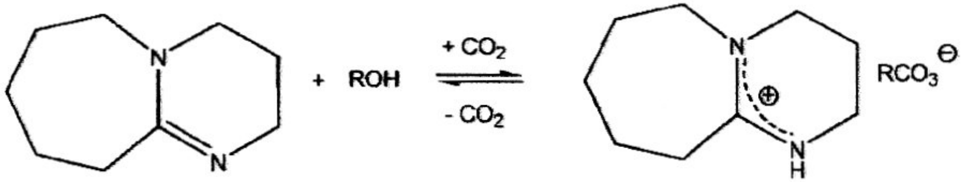


- low ionic strength
- low osmotic pressure
- good solvent for polar organics

- high ionic strength
- high osmotic pressure
- poor solvent for polar organics

Amidines and guanidines

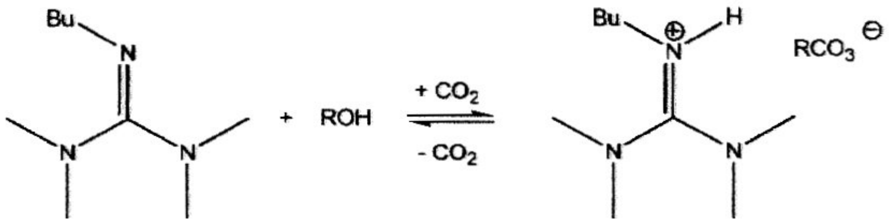
Reversible switch from a molecular liquid mixture of **DBU** or **TMBG** and ROH to the ionic liquid [DBUH]+[RCO_3] and [TMBGH]+[RCO_3] upon addition of CO_2, respectively.



Green Chem. **2010**, *12*, 809-814

Log K = 1.7

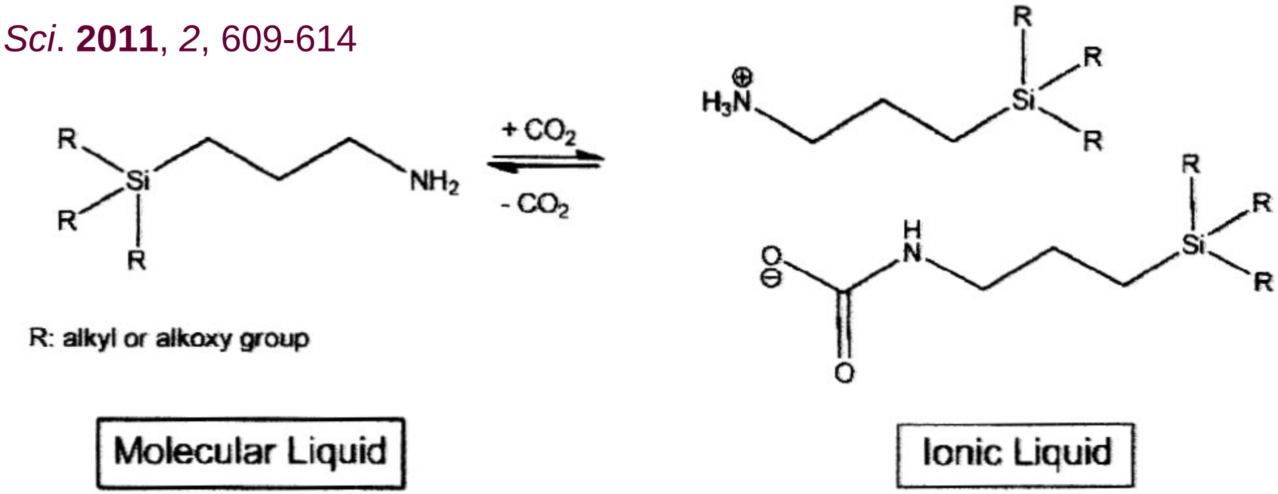
Log K = 3~7

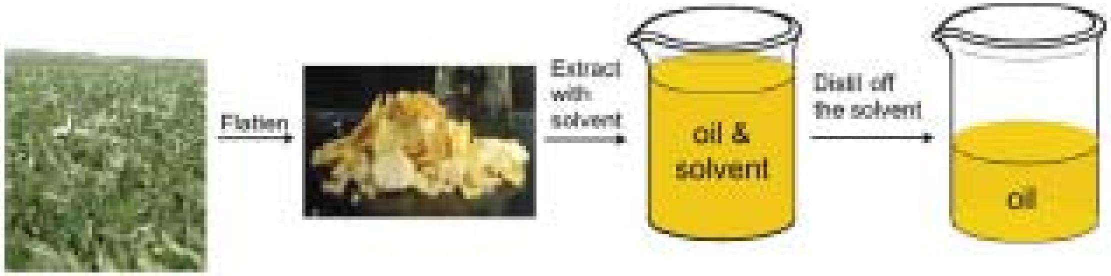


R = C_1 to C_{12}.

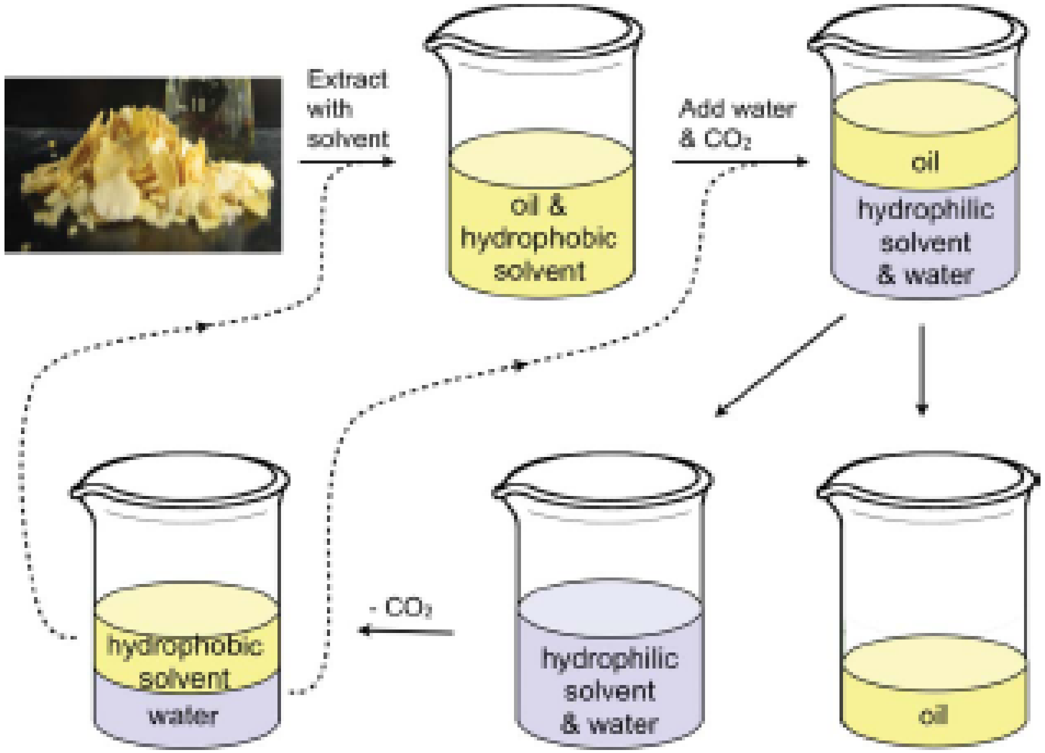
One-component system: reversible switch from a molecular liquid **trialkoxy- and trialkyl-silylpropylamine** to its corresponding ionic liquid upon addition of CO_2.

Chem. Sci. **2011**, *2*, 609-614





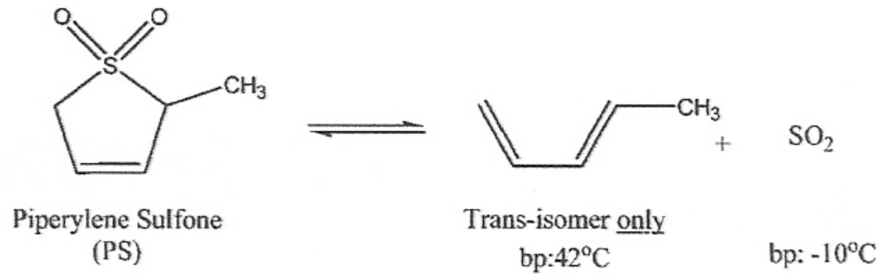
Conventional method for obtaining soybean oil after distillation

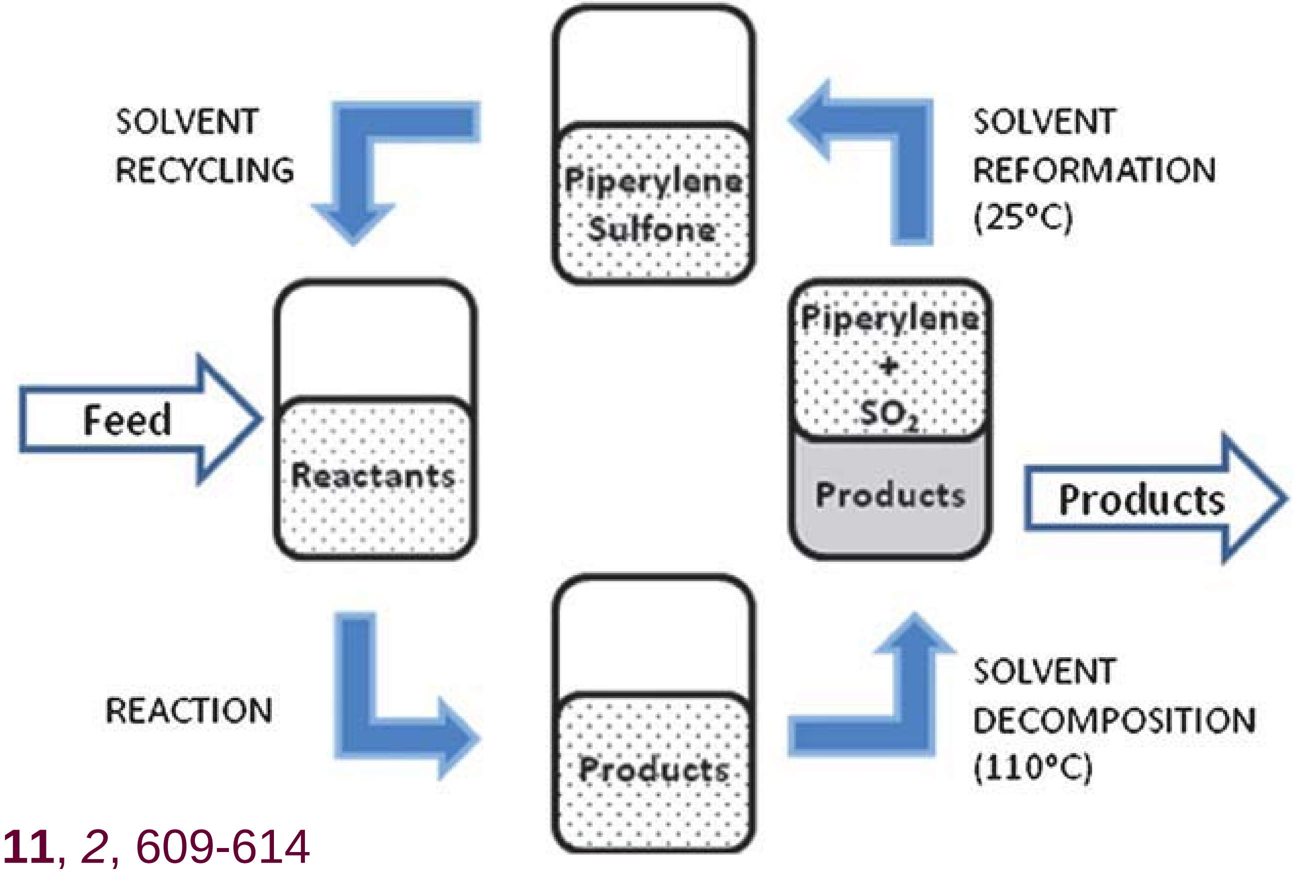


The use of SHS method avoids distillation

Green Chem. **2010**, *12*, 809-814

Switchable solvent and recycling





Chem. Sci. **2011**, *2*, 609-614

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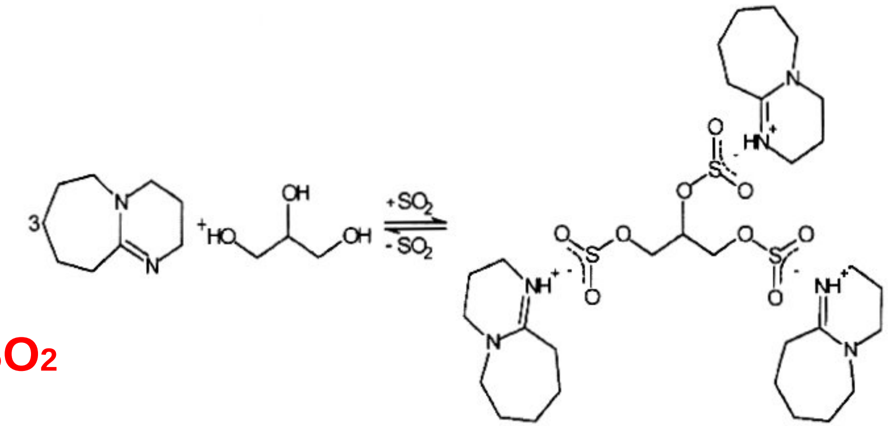
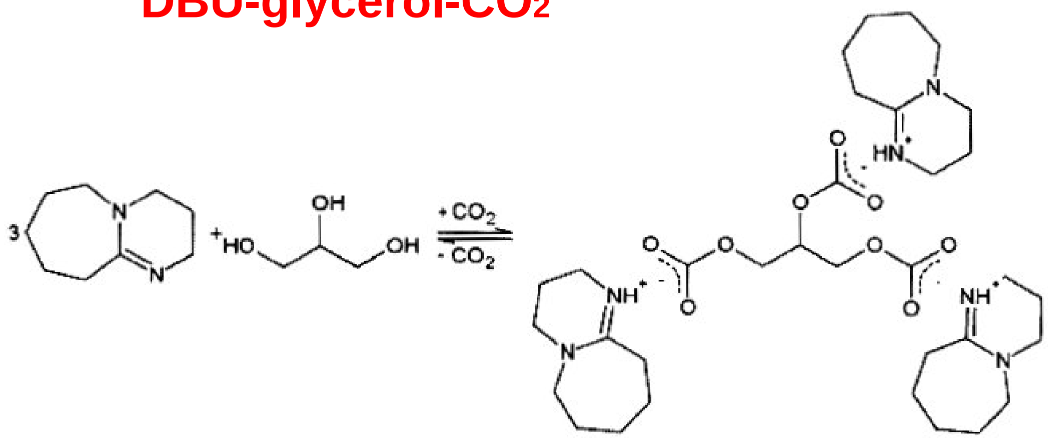
Switchable Ionic Liquids



DBU-glycerol-SO_2

Scheme 3 Proposed mechanism for the formation of SIL2, DBU-glycerol-SO_2.

DBU-glycerol-CO_2



(*RSC Advances* **2011**, *1*, 452-457)

Scheme 2 Proposed mechanism for the formation of SIL1, DBU-glycerol-CO_2.

Challenges in searching for green solvents

- Polarity vs. basicity
- Environmentally Benign (including manufacture)
- Easy to move (recover)
- Eliminating distillation

(Jessop, *Green Chem*. **2011**, *13*, 1391-1398)

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Sustainability of chemistry and engineering can only be achieved by sustainable chemistry and engineering

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