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]。

十二原則的介紹/業界實例

孕育永續必需綠色化學, 12項原則是從業者需了然於胸的執行面圭臬

2014年11月22日 14:10 – 14:40

中興院區51館 2C會議室

甘魯生 教授 lskan@gate.sinica.edu.tw
中央研究院兼任研究員
綠色/永續化學工作坊講員 (2010-2014)
國科會化學中心永續/綠色化學通訊 編輯 (2011)
大同大學生物工程學系綠能及綠色化學月刊 顧問 (2010-2011)
大同大學 講座教授 (2008-2010)
財團法人傑出人才基金會傑出人才講座

難題和對策

人口增加導致能源枯竭、糧食短缺
有毒物質累積導致氣候變遷、飲用水被污染

綠色化學：設計化學產物(肥料、除蟲/草劑、民生用品等)及製造過程時要減少或消除廢物及有毒物質之產生並符合經濟原則。

綠色化學12項原則 摘自 Green Chemistry: Theory and Practice, Anastas, P. T.; Warner, J. C., Oxford University Press: New York, 1998, p.30.

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

英文創意版 摘自S. L. Y. Tang, R. L. Smith, and M. Poliakoff, Principles of green chemistry: PRODUCTIVELY, Green Chem., 2005 7, 761-762.

Condensed Principles of Green Chemistry

P - Prevent wastes
R - Renewable materials
O - Omit derivatization steps
D - Degradable chemical products
U - Use safe synthetic methods
C - Catalytic reagents
T - Temperature, Pressure ambient
I - In-Process Monitoring
V - Very few auxiliary substances
E - E-factor, maximise feed in product
L - Low toxicity of chemical products
Y - Yes, it is safe

12項原則系列影片

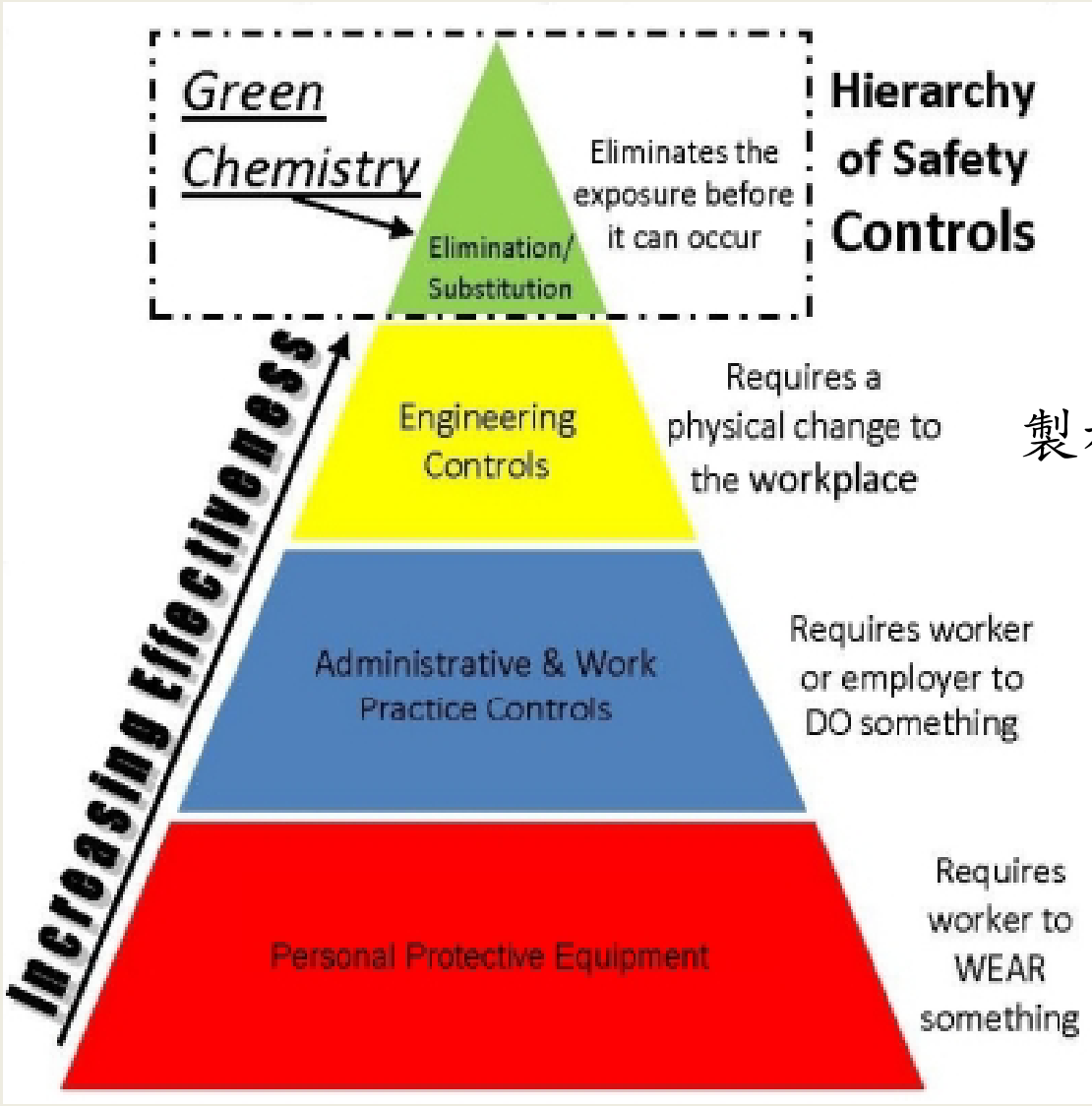
http://www.ecy.wa.gov/programs/hwtr/p2/GreenChem/TwelvePrinciples.html

Introduction	*http://vimeo.com/69592688*	*David Constable*	*21 ′*
Part I	*http://vimeo.com/69719190*	*Richard Williams*	*21′*
II	*http://vimeo.com/69719191*	*David Constable*	*20′*
III	*http://vimeo.com/69719193*	*Richard Williams*	*21′*
IV	*http://vimeo.com/69719192*	*Richard Williams*	*13′*
V	*http://vimeo.com/70057858*	*David Constable*	*21′*
VI	*http://vimeo.com/70057859*	*David Constable*	*21.5′*
VII	*http://vimeo.com/70233370*	*Richard Williams*	*15′*
VIII	*http://vimeo.com/77950968*	*David Constable*	*18′*
IX	*http://vimeo.com/77950962*	*David Constable*	*24′*
X	*http://vimeo.com/77950964*	*Richard Williams*	*19′*
XI	*http://vimeo.com/77950965*	*David Constable*	*20′*
XII	*http://vimeo.com/77950967*	*David Constable*	*21′*
Conclusion	*http://vimeo.com/70233369*	*David Constable*	*19′*

綠色化學十二原則之中譯 附標題

1. **避免廢料：** 設計化學合成使之避免廢料，不產生需處理或清理的廢料。
2. **發揮最大的原子經濟：** 設計合成使得終極產物含有最大部分的原始反應料。而沒有甚麼浪費的原子。即便有也是很少。
3. **低危險的化學合成：** 無論在何地，只要實際可行，合成方法應設計成用的原料及製出的成品都無害於人類健康和環境，或是毒性很低。
4. **設計更安全的化合物：** 化學產品應設計成能在使它們的毒性縮到最小下實現達到所希望賦與的功能。
5. **更安全的溶劑和輔助劑：** 有關(化學合成)的輔助物質(即： 溶劑、分離劑等)儘可能不用，若用也要是無害的。
6. **為用能效率而設計：** 化學過程中能的需求應該被認定為對環境和經濟的衝擊縮為最小。如果可能，合成方法應該在常溫和常壓下進行。
7. **使用可再生的原料：** 祇要技術和經濟可行時儘量用再生而非消耗的生物料和原料。
8. **減少衍生物：** 儘可能減少或避免不需要的衍生反應(阻擋基、保護物/去保護物、物理/化學過程中之暫時修飾)，因為此步驟需額外的試劑和產生廢料。
9. **催化作用：** 儘可能使用有選擇能力之催化劑，且優先於使用化學當量的試劑。
10. **為分解而設計：** 化學產物的設計應考慮到當它們的功能結束時會分解為無害的降解物而不會存留在環境中。
11. **即時分析以防止污染：** 發展出能即時和在線上監控和管理的分析方法，使在危險物質發生之前及時得到訊息，防止污染。
12. **本質上更安全的化學以防止意外：** 在化學反應中由一物質形成另一物質應該選擇能縮小化學意外的途徑，包括釋出(能)、爆炸及火災之可能性。

防範未然優於事後處理 第11,12項



綠色化學能在源頭上防止災害

製程及工作環境改善

防災訓練

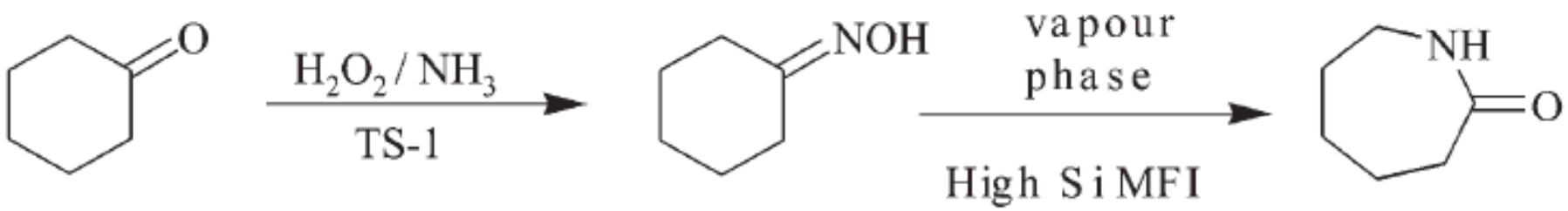
個人保護

綠色化學之精義在於..

減少、降低或免除

- 廢物
- 物質
- 災害
- 風險
- 用能
- 成本

住友化學合成尼龍6原料Caprolactam



Ammoximation　　Beckmann rearrangement

Current process:

$$C_6H_{10}O + 0.5(NH_3OH)_2SO_4 + 1.5H_2SO_4 + 4\ NH_3 \longrightarrow C_6H_{11}NO + 2\ (NH_4)_2\ SO_4$$

Atom efficiency =29% ;　E = 4.5

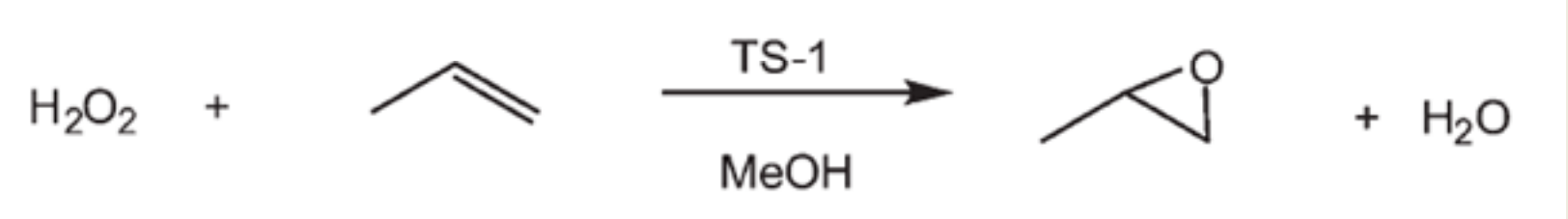
New process Sumitomo Chemicals (住友化學株式會社)

$$C_6H_{10}O + H_2O_2 + NH_3 \longrightarrow C_6H_{11}NO + 2H_2O$$

Atom efficiency = 75% ; E = 0.32 (<0.1)

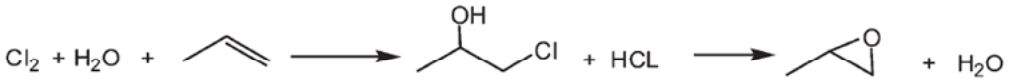
Enichem的propylene oxide綠色製法

Propylene oxide是polyurethane (聚氨酯,PU)的原料.PU是黏合劑、塗層！低速輪胎、墊圈、車墊等工業領域、各種泡沫和塑料海綿和醫用器材。



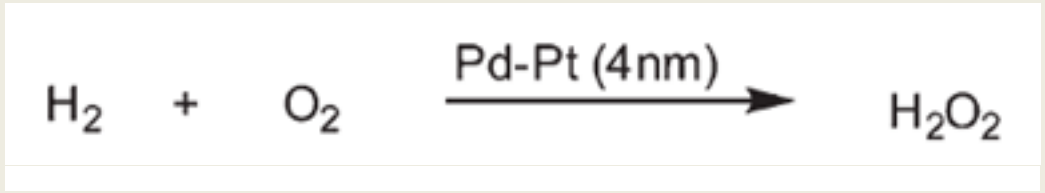
2007年較綠之反應條件總統挑戰獎

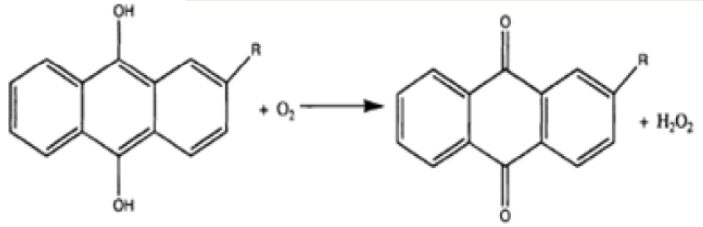
1. Chlorohydrin route



2. Hydroperoxide (coproduct) processes

R = t-Bu , $PhCH(CH_3)$- , $PhC(CH_3)_2$-





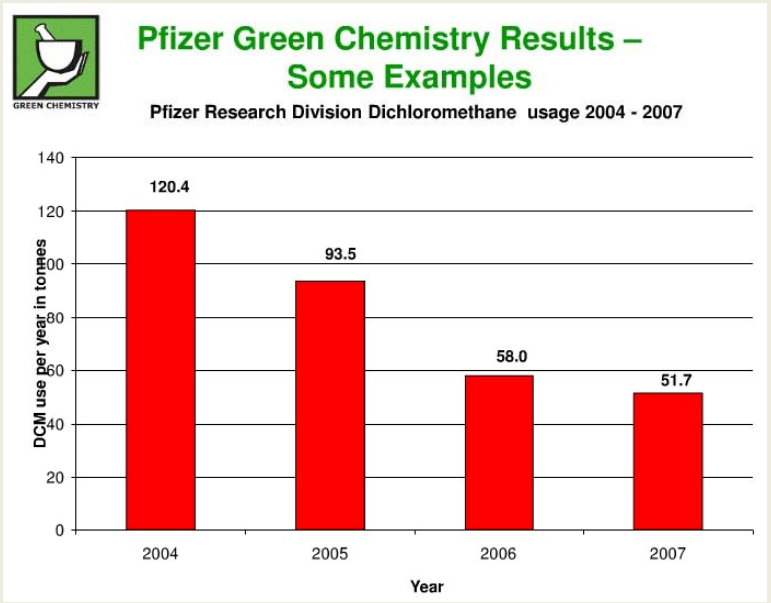
Synthesis of hydrogen peroxide from Anthraquinone

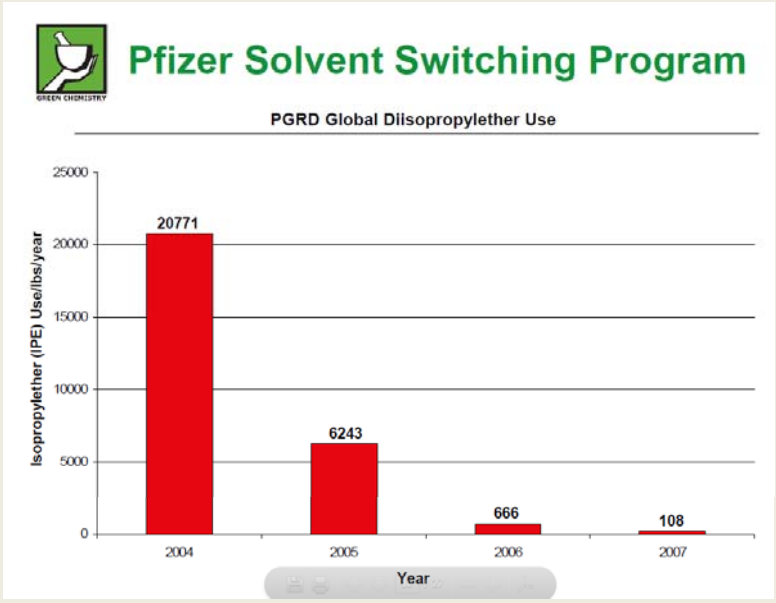
Headwaters Technology Innovation
Direct Synthesis of Hydrogen Peroxide by Selective Nanocatalyst Technology

Pfizer公司溶劑置換表及成果

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 or carbon tetrachloride	Dichloromethane
Dimethyl formamide, dimethyl acetamide or *N*-methylpyrrolidinone	Acetonitrile
Pyridine	Et_3N (if pyridine used as base)
Dichloromethane (extractions)	EtOAc, MTBE, toluene, 2-MeTHF
Dichloromethane (chromatography)	EtOAc/heptane
Benzene	Toluene

K. Alfonsi, *et al.*, *Green Chem*. **2008**, *10*, 31-36





http://www.dbu.de/media/130508051211a525.pdf

工業界實用範例 摘自周德璋『綠色化在化學與製藥工業之應用』中國化學年會"綠色化學工作坊", 11/30/2011 http://gc.chem.sinica.edu.tw/learn.html

Case 1.

Pregabalin (Lyrica®)

A Drug for the treatment of Neuropathic Pain

Case 2.

Sildenafil Citrate

The Active pharmaceutical ingredient (API) in the PDE_5 Inhibitor Viagra™

Case 3.

Ibuprofen

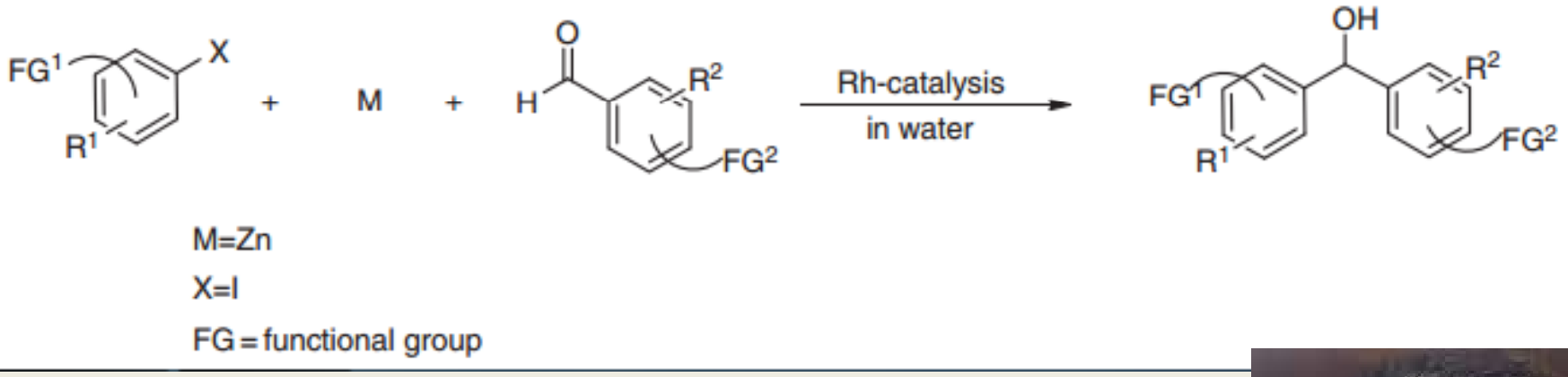
One of core non-steroidal anti-inflammatory medicines

Case 4.

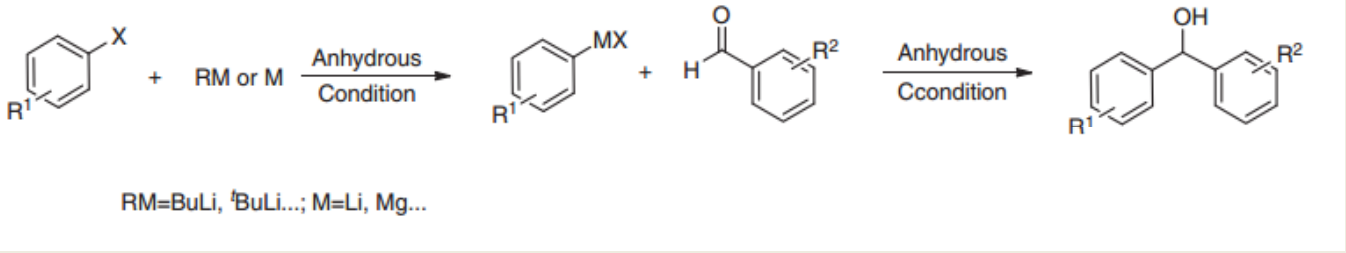
Disodium iminodiacetate (DSIDA)

A key intermediate in the production of Roundup® herbicide

最友善的溶劑: 水 摘自Feng Zhou1 & Chao-Jun Li, The Barbier–Grignard-type arylation of aldehydesusing unactivated aryl iodides in water, NATURE COMMUNICATIONS 2014 | 5:4254 | DOI: 10.1038/ncomms5254



Barbier–Grignard-type in water



Traditional Barbier–Grignard-type

Chao-jun Li, 李兆俊

Chunmei Wei and Chao-Jun Li, **Grignard type reaction *via* C–H bond activation in water,** *Green Chem.*, 2002, 4, 39-41

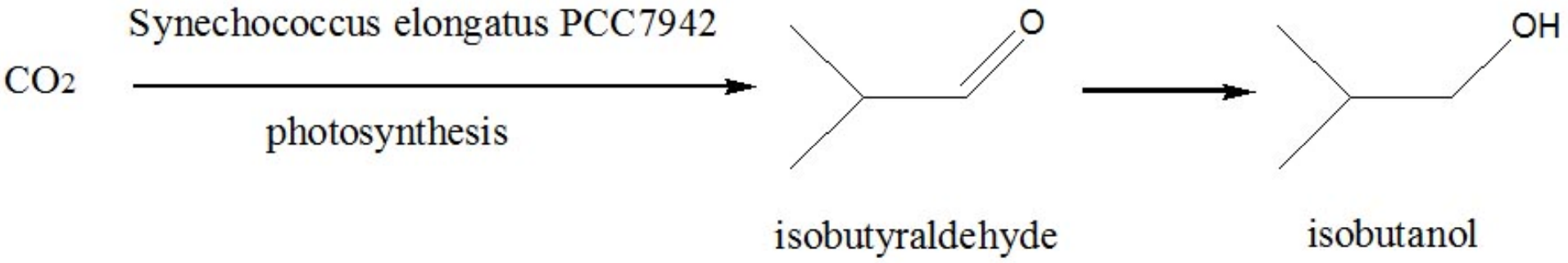
回顧論文(1) Li, C.-J., "Organic Reactions in Aqueous Media with a Focus on Carbon-Carbon Bond Formation", Chem. Rev., (1999), 93, 2023-2035; (2) Li, C.-J., "Organic Reactions in Aqueous Media with a Focus on Carbon-Carbon Bond Formations: A Decade Update", Chem Rev., (2005), 105, 3095-3165.

書 (1) Li, C.-J., "Organic Reactions in Aqueous Solution", John Wiley, 1997. (2) Li, C.-J., Chan, T.-H., "Comprehensive Organic Reactions in Aqueous Media", 2nd ed., Wiley- Interscience, 2007.

省能: 跳出傳統的思維 摘自甘魯生『綠色製程實驗方法與實例』中國化學年會 "綠色化學工作坊", 11/23/2013

非傳統方法	反應物之必要條件
微波反應 (Microwave)	極性或解離物質
微觀尺寸流動 反應(Microflow)	溶液
超音波化學 (Sonochemistry)	溶液
機械化學(Mechanochemistry)	固體
電化學(Electrochemistry)	導電
光化學(Photochemistry)	發色團(chromophore)

改良光合作用:將二氧化碳轉變為柴油



CO_2 emissions in 2006 were 29 billion metric tons, an increase of 35% from 1990
atmospheric levels of CO_2 have increased by ~25% over the past 150 years
二氧化碳是眾所週知的溫室氣體.吾人正因它的逐漸增加所引起各種自然災害而煩惱.現能反其道而行將二氧化碳轉變為燃料和其他化學原料.而且其過程(光合作用)是非常乾淨.碳數比乙醇高的醇的含能量高、吸水性低、蒸氣壓低(不易污染空氣)等優點.如果每年能生產600億加侖(約佔25%之汽油)就可以去除500百萬噸二氧化碳,這數字約等於全美國一年二氧化碳排放量之8.3%.
2010總統綠色化學挑戰獎(四) —學術獎得主James C. Liao教授

Nature Biotechnology **27**, 1177 - 1180 (2009)
綠能及綠色化學第五期. (http://www.bioeng.ttu.edu.tw/issues/issuesindex.html)
Presidential Green Chemistry Challenge Award:
http://www.epa.gov/gcc/pubs/pgcc/presgcc.html

廖俊智院士

http://www.chemeng.ucla.edu/people/faculty/james-c-liao

友善的金屬催化劑: 鈣離子 摘自Calcium catalyzed hydroalkoxylation. Anastasie Kena Diba, Jeanne-Marie Begouin, Meike Niggemann, Tetrahedron Letters 53 (2012) 6629–6632

γ,δ-unsaturated alcohols

5 mol-% $Ca(NTf_2)_2$ and 5 mol-% Bu_4NPF_6

→

room temperature

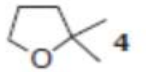
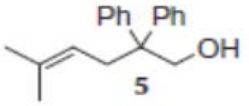
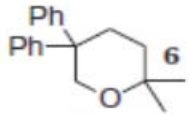
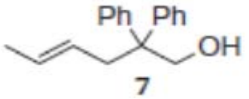
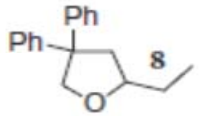
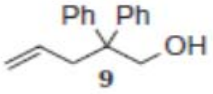
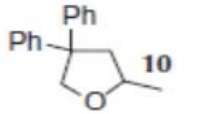
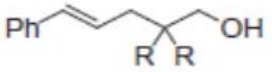
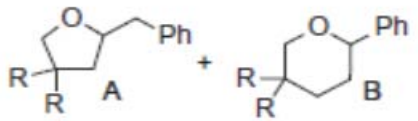
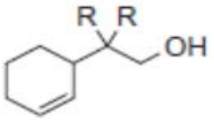
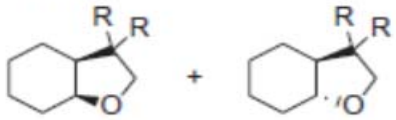
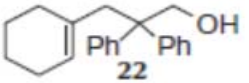
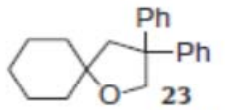
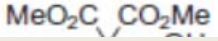
cycloisomerization

Full regioselectivity is observed in all transformations

$Ca(NTf_2)_2$ **Calcium(II) bis(trifluoromethanesulfonimide)**

Bu_4NPF_6 **Tetrabutylammonium hexafluorophosphate**

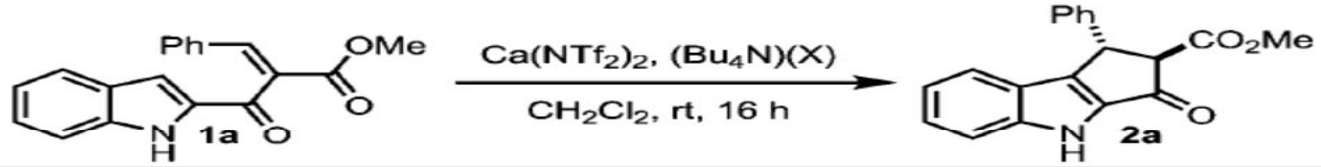
Table 2
Cyclization of different alcohols

Entry[a]	Alcohol	Product	t	Yield[b] (%)
1			2 h	96
2			1 h	85
3[c]			24 h	82
4			24 h	81
5[c] 6[c] 7	 R = Ph (**11**) R = Me (**13**) R = H (**15**)	 A (**12**) B (**14**) B (**16**)	 20 h 20 h 20 h	 96 97 81
8 9[c] 10	 R = Ph (**17**) R = Me (**19**) R = H (**21**)	 *cis:trans* 98:2 (**18**) *cis:trans* 98:2 (**20**) –	 2 h 20 h 24 h	 80 9 –
11			1.5 h	82
				

友善的金屬催化劑: 鈣離子 (續)

Chem Commun (Camb). 2014 Nov 6;50(96):15171-4. doi: 10.1039/c4cc06501h.
The first calcium-catalysed Nazarov cyclisation. Davies J, Leonori D.

A)

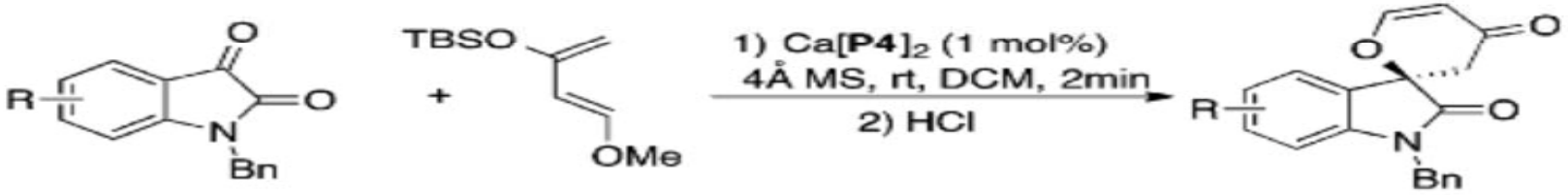


Entry	$Ca(NTf_2)_2$	$(Bu_4N)(X)$	Yield (%)	dr	Entry	$Ca(NTf_2)_2$	$(Bu_4N)(X)$	Yield (%)	dr
1[a]	**5 mol%**	**PF_6; 5 mol%**	**87**	**94:6**	**6**	5 mol%	BF_4; 5 mol%	21	94:6
2	1 mol%	PF_6; 1 mol%	62	94:6	**7**	5 mol%	$SiPh_3F_2$; 5 mol%	<5	nd
3	5 mol%	–	–	–	**8**	5 mol%	I; 5 mol%	9	nd
4	–	PF_6; 5 mol%	–	–	**9**	5 mol%	Br; 5 mol%	<5	nd
5	–	NTf_2; 5 mol%	–	–	**10**	5 mol%	OTf; 5 mol%	–	–

a The reaction time was 6 h; nd: not determined

Chem Commun (Camb). 2014 Oct 21;50(91):14187-90. doi: 10.1039/c4cc06520d.
Chiral metal phosphate catalysis: highly asymmetric hetero-Diels-Alder reactions.
Liang T, Li G, Wojtas L, Antilla JC.

Table 3 Asymmetric HDA reaction of isatin



4a-f **2** **5a-f**

Entry	R	5	Yield[a] (%)	ee[b] (%)
1[c]	H	5a	95	98

中文創意版 摘自趙奕姈『綠色化學之發展與應用』逢甲大學"綠色化學與清潔製程論壇" 2014/5/2

中文綠色化學十二原則

1. 防廢：預先減廢總勝於事後清理廢物
2. 物盡：化學合成應注重原子經濟效率
3. 低毒：合成方法應選無毒或低毒物料
4. 保安：化學產品必須兼顧效能及環安
5. 降輔：降低輔助化學品的使用或毒害
6. 節能：合成多選常溫常壓的節能程序
7. 再生：用再生物料優於技術經濟實惠
8. 簡潔：少用複雜的衍生物劑料或反應
9. 催化：高選擇催化程序優於計量反應
10. 可解：化學產品須能降解成無害物質
11. 監測：開發工廠即時毒物監測分析法
12. 思危：設計化學程序需居安思危遠見

廢物低
保降能
再簡化
可監危

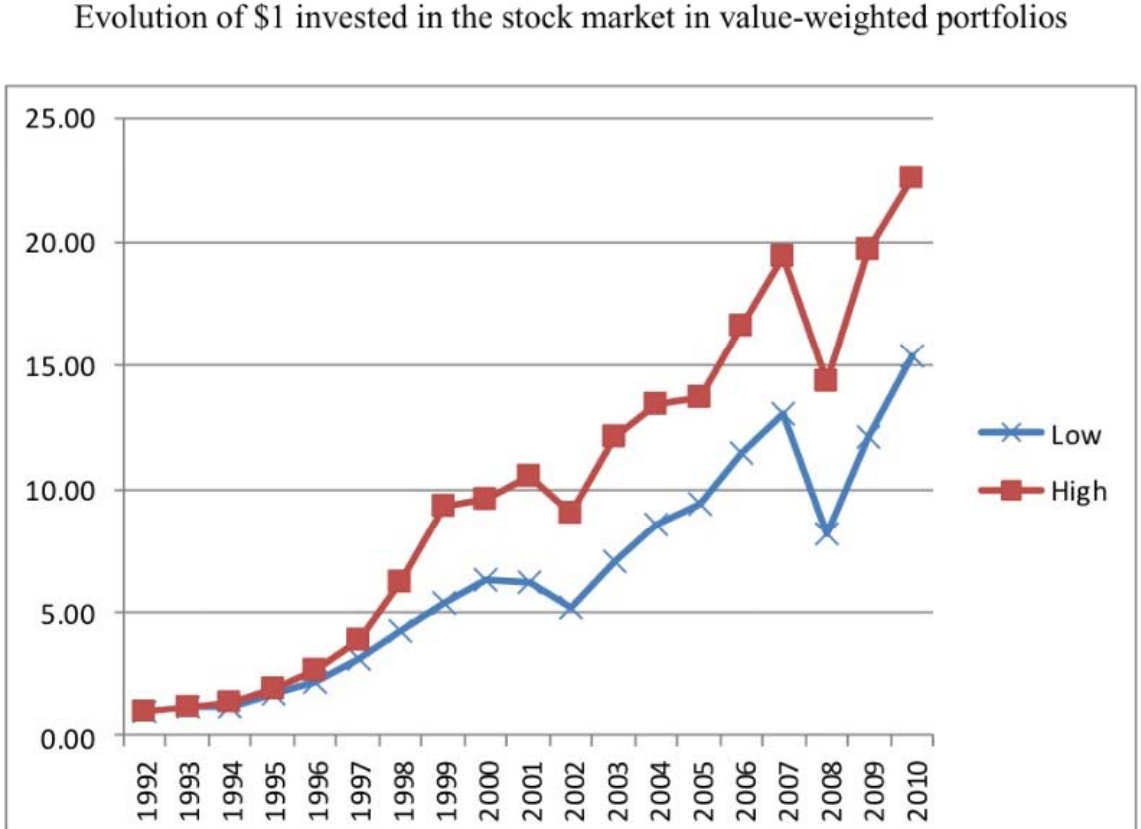
蔡蘊明：陳竹亭

我們的努力..

綠色I永續化學網路資共享網
http://gc.chem.sinica.edu.tw/
綠色I永續化學網路資共享網通訊
http://gc.chem.sinica.edu.tw/learn.html
綠色I永續合成化學工作坊歷年講義
http://gc.chem.sinica.edu.tw/workshop/notes.php
『綠能及綠色化學電子月刊』
http://www.bioeng.ttu.edu.tw/issues/issuesindex.html

不可阻擋的趨勢

A 2012 survey by Independent Chemical Information Services (ICIS) shows 54% of 700+ respondents say their company has a sustainability strategy and /or policy already in place, and a further 17% indicate a policy is currently in development and 17% that initiatives are likely within the next 2-3 years. Only 12% reported that there is little interest. http://img.en25.com/Web/ICIS/FC0126_Chem_201301.pdf



Paul Anastas: "We can, I believe we will, because we must."

http://www.hbs.edu/faculty/Publication%20Files/12-035_a3c1f5d8-452d-4b48-9a49-812424424cc2.pdf

對化學工業及化學家的期望和化學工作者自我認知

對化學工業及化學家的期望

對社會、環境及經濟是責無旁貸
化學技術要日新又新、精益求精
化學製造要對社會及環境負責
推廣教育,喚醒大眾對環境保護的認知

化學工作者自我認知

全球變遷的腳步在加快中.
綠色化學能產生新一代的安全物品,而且是創新的和具競爭力的.
綠色化學要從分子開始設計健康的,永續的產品.
重新設計對環境健康的安全產品有無限商機.
將現有的商品從市場上去除有時是非常困難的事,所以把握綠色化學的原則至為要緊.

“Delicate motion should reside in all ordinary things around us, revealing itself only to him who looks for it”, E. M. Purcell

未來思考方向

學生:　　要自動自發學習綠色/永續化學

工程師:　要有綠色/永續化學素養

化學教授:要積極發現及學習綠色/永續化學新方法並融入研究及教學中

研發人員: 要影響管理階層綠色/永續化學是有報酬及利潤的

創新及研究:要以落實於應用為終極目標

誌謝

綠色/永續合成化學工作坊
趙奕姈 周德璋
中國化學會環境委員會
科技部化學研究推動中心

謝謝大家