

THE GREEN ORGANIC CHEMISTRY

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ABSTRACT

The pollution disaster is a major problem all around the world. It has unfavorably affected the lives of millions of people and caused many deaths and health disorders. A *pollutant* is any substance that, when in an environment, poisons our air, land and water. Chemicals have poisoned all of the world, harming humans, wildlife, and plant life, on land, sea and air. About one hundred thousand synthetic chemicals are now on the market, with approximately one thousand new chemicals are added yearly.

Although companies test the toxicity of their products individually, they do not exist alone in the environment. Compounds are altered in combination with others, but the effect of these combinations are not tested or studied. Pesticides, designed to kill insects, weeds and fungus, are also toxic to human nervous systems, and are linked to reproductive, developmental, neurological and immune-system damage. Every chemical we use, every substance we produce, in manufacturing, farming, energy use, or consumption, remains here on Earth. These pollutants poisons seems to be disappeared, in facts, they were only hidden.

Chemical products can be manufacture using a wide variety of synthesis routes. The designer of a chemical process must choose from alternative raw materials, solvents, reaction pathways, reaction conditions, and these design choices can have a significant impact on the overall environmental performance of a chemical process.

In many ways, green chemistry is a philosophy and a way of thinking. It is not a new branch of chemistry but is a pulling together of tools, techniques and technologies that can help chemists in research and production to develop more eco-friendly and efficient products and processes.

Green chemistry is both the chemistry of the future and the chemistry of today. It is based on, a number of principles that ensure that both processes and final-products are clean and safe. Green chemistry protects the environment, not by cleaning it up, but by inventing new chemistry and new chemical processes that do not pollute.

Green Chemistry is the utilization of a set of principles that reduces or eliminates the use and/or generation of hazardous substances in the design, manufacture, and application of chemical compounds. It aims to replace hazardous reagents with safer renewable reagents; minimize or eliminate the generation of hazardous waste and products, avoid auxiliary substances, such as solvents and catalytic reagents, whenever possible.

In a little while, it is clear that, the rules of the green chemistry will not be enough to prevent the environment; it is time to search an effective strategy to save our world.

1. Global situation analysis 1995 and prognoses for 2040:

In the year 2040 we will have to feed 9–10 billion people and to provide them with energy and materials. We want them to live according to the requirements of a developed society, and we do not want to pollute the earth or change the climate. The question addressed in this contribution is whether this scenario -sustainable technological growth- is technologically possible on a world wide basis. In 1996, more than 80% of the world's energy demands originated from fossil resources (mineral oil, coal and gas) and the same holds for organic raw materials (Okkerse and Van Berkkum, 1999).

The stocks of fossil resources are finite. First of all, mineral oil stocks will be exhausted around 2050 if we continue our present way of life. All kinds of pollution from global warming to acid rain, from smog to ground water pollution, have been linked to our environmental considerations and how can be eliminate or reduce the risk of the industrial processes, specially the chemical industries processes.

Our natural resources are the sun, CO₂ in the atmosphere and land and water on the earth. In Table (1) some critical global data are given. The fundamental questions arising from these data are whether it is at all possible, without fossil resources, to produce sufficient food

(1st priority), organic materials (2nd priority) and energy (3rd priority) to allow 9–10 billion people a decent life (Okkerse and Van Berkum, 1999).

Table (1): Situation analysis 1995 and prognosis for 2040

Critical global data:	1995	2040
Population	5×10^9	10×10^9
Energy consumption/EJ	350	900
Agricultural land/hectar	3.4×10^9	2.8×10^9
Organic materials/ton	0.3×10^3	1.0×10^3

The present-day commercial energy demands are mainly (85%) met by fossil fuels (oil *ca.* 40%, coal *ca.* 25%, gas *ca.* 20%). Nuclear energy contributes about 5%, the same figure applies for hydroelectric power. The remaining 5% is divided over renewable sources such as biomass, solar energy, wind, *etc.* Some 14% of the energy consumption consists of non-commercial energy, mainly in the developing world, from biomass (straw, sugar cane, *etc.*).

Point Source and Nonpoint Source Pollution :-

Pollution sources are classified as *point source* or *nonpoint source*. Point source pollution comes from a particular place such as industrial and sewage treatment plants. Non-Point source pollution occurs when rainfall or snow melt moving over and through the ground, picks up natural and human-made pollutants and finally deposits them into lakes, rivers, wetlands, coastal waters, and even our underground sources of drinking water.

2. Introduction to GREEN CHEMISTRY

2.1. The definition of the Green Chemistry:

In most countries the general public associate the word ‘green’ with ‘all things good for the environment’. The ‘green’ word is also representative of a certain political philosophy in some countries.

So what is Green Chemistry?

The term “**Green Chemistry**”, as adopted by Paul Anastas, Industrial Chemistry Branch Chief for the Environmental Protection Agency (EPA), first coined the phrase “green chemistry” back in 1992

and also as adopted by the IUPAC Working Party on Synthetic Pathways and Processes in Green Chemistry, is defined as: “ The invention, design, and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances”.

2.2. The Twelve Principles of Green Chemistry:

The EPA issued 12 principles of Green Chemistry, which go somewhat in explaining what the definition means in practice (Lancaster, 2000). The principles cover such concepts as: (1) Prevention (2) Atom Economy (3) Less Hazardous Chemical Synthesis (4) Designing Safer Chemicals (5) Safer Solvents (6) Design for Energy Efficiency (7) Use of Renewable Feedstocks (8) Reduce Derivatives (9) Catalysis (10) Design for Degradation (11) Real-time Analysis for Pollution Prevention (12) Inherently Safer Chemistry for Accident Prevention

2.4. Some atom economic and atom un-economic reactions

By taking the atom economy of various synthetic routes into account at the planning stage the chosen strategy is likely to produce a greater weight of products per unit weight of reactants than might otherwise have been the case. There are, however, a number of common reaction types which are inherently atom efficient and a number, which are not (Table 2).

Table (2): Some atom economic and atom un-economic reactions.

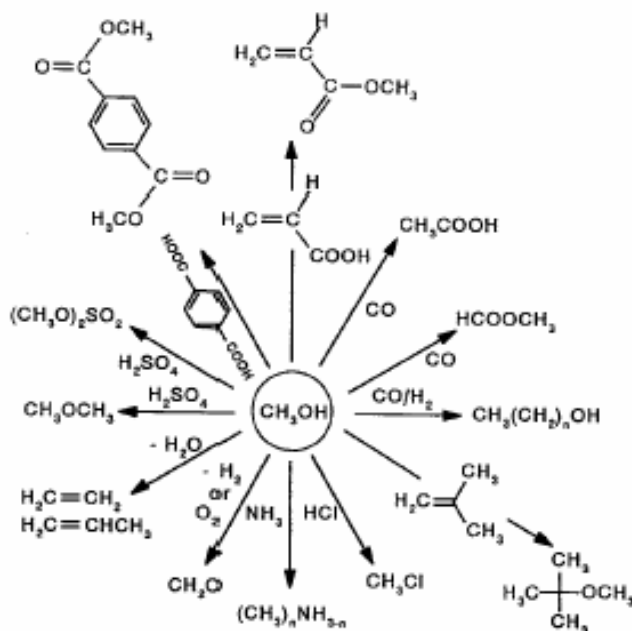
Atom economic reactions	Atom un-economic reactions
Rearrangement	Substitution
Addition	Elimination
Diels-Alder	Witting
Other concerted reactions	Grignard

3. The Green Chemistry applications in the organic Chemistry:

3.1. Hydrogen as a chemical Key:

In a scenario without fossil fuel, solar energy may also be the starting point of a hydrogen economy by electrolysis of water. Hydrogen gas is a clean and powerful fuel. Also, hydrogen is important in making NH_3 . As stated before, solar energy can lead

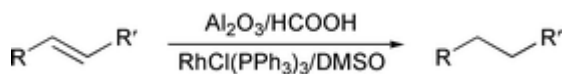
directly to H_2 as a key chemical for many applications. H_2 may be used as such (*e.g.*, fuel in space shuttles) or stored in metals such as Pd. Hydrogen can also be stored chemically by reaction with, *e.g.*, CO_2 to CH_3OH . In turn, CH_3OH is a very good liquid fuel and a key chemical in the production of many organic chemicals (Okkerse and Van Berkkum, 1999). Scheme (1) shows the versatility of methanol as a starting compound.



Scheme (1): Methanol as a key chemical.

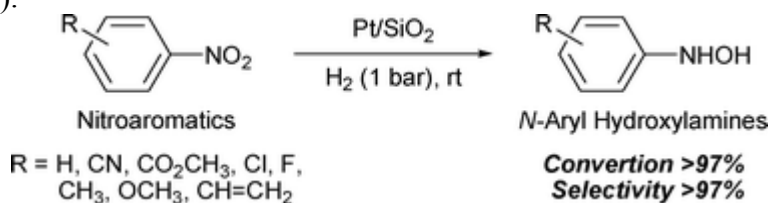
In conclusion, H_2 is a powerful energy carrier and, *via* methanol, an essential starting material for (bulk) chemicals. Therefore, we may witness the start of a hydrogen-based economy, together with the plant-based economy.

Under microwave and thermal conditions hydrogenation of alkenes may be achieved in excellent yields using a cheap recyclable transfer hydrogenation source supported on alumina in presence of Wilkinson's catalyst (Danks and Desai, 2002).

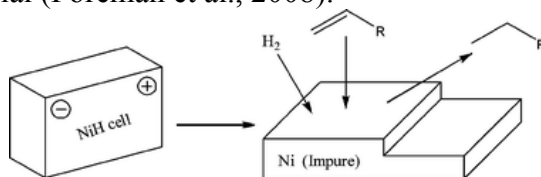


The thermal decomposition of HCO_2H or preferably, HCO_2X ($\text{X} = \text{Na}$ or NH_4) can be used to generate H_2 for the continuous hydrogenation of aromatic and cyclic aldehydes, ketones and nitroaromatics in high temperature pressurised water (HTPW). This means that hydrogenation reactions can be carried out in exactly the same equipment as has previously been used for selective oxidation in HTPW, thus facilitating relatively simple application of these reactions for non-specialists (Verdugo et al., 2006).

Various substituted nitroaromatics were successfully hydrogenated to the corresponding *N*-aryl hydroxylamines in excellent yields (up to 99%) using supported platinum catalysts such as Pt/SiO_2 under a hydrogen atmosphere (1 bar) at room temperature (Takenaka, 2008).



A synthesis of a safe and effective hydrogenation catalyst has been developed with used nickel metal hydride electrical cells as the starting material (Foreman et al., 2008).



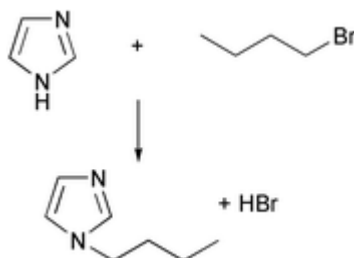
Ceria-based catalysts are good candidates for integrating methane combustion and hydrogen generation. These new, tuneable catalysts are easily prepared. They are robust inorganic crystalline materials, and perform well at the $400\text{ }^\circ\text{C}$ – $550\text{ }^\circ\text{C}$ range, in some cases even without precious metals. This makes them attractive for practical applications in the energy conversion market (Beckers et al., 2009).

Red mud, a waste product of the aluminium industry, has been shown to possess significant activity for the decomposition of methane, a by-product of oil refining and landfill, generating hydrogen and a carbon containing magnetic material. It is envisaged

that the latter material could be of interest in terms of downstream purification processes and that its magnetic properties may facilitate separation/handling. In this way, two valuable end products can be generated from two waste products (Balakrishnan *et al.*, 2009).

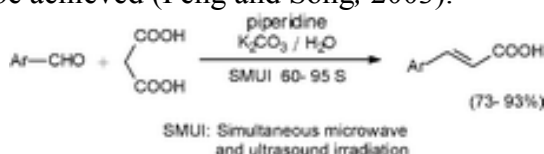
3.3. Ultrasound:

The synthesis of N-substituted imidazoles *via* alkylation of imidazole with 1-bromobutane by sonochemical and thermally-activated reactions over two alkali-metal promoted carbons (Na^+ - and Cs^+ -Norit) as catalysts was reported by Lopez-Pestaña *et al.* (2002).

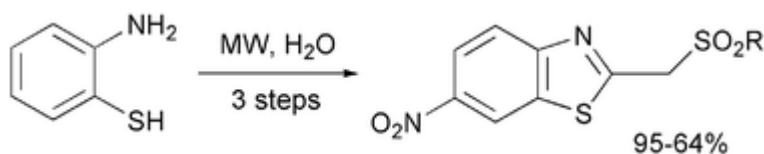


The *O*-acetylation of alcohols with acetic anhydride to the corresponding esters has been achieved in excellent isolated yields in short reaction time at ambient conditions under ultrasonic irradiation in the absence of any added catalyst using a room temperature ionic liquid as the medium as well as a promoter for the reaction. The products could be isolated by distillation or selective extraction from the non-volatile ionic liquid, which could be recycled giving rise to a process with minimal waste (Gholap *et al.*, 2003).

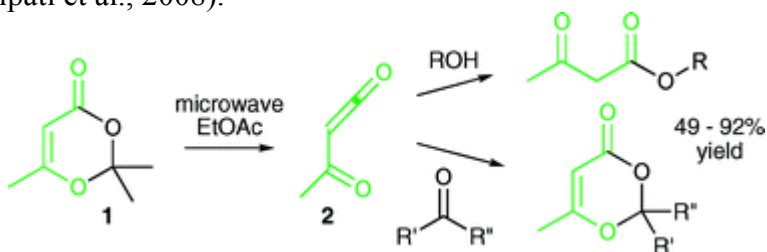
The microwave and ultrasound combined aqueous Knoevenagel–Doebner reaction proves an efficient and eco-friendly route for preparing 3-aryl acrylic acids in good yields. This organic solvent-free protocol is valuable since rapid reaction rate, low energy consumption, waste minimization, simple operation and easier product work-up can be achieved (Peng and Song, 2003).



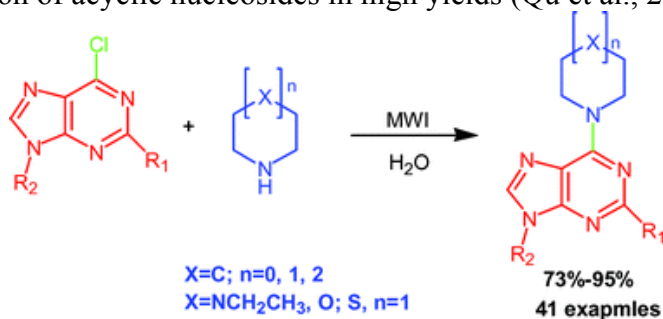
A clean, rapid and energy-efficient approach to solid–aqueous heterogeneous reactions was developed utilizing the synergistic effect



Microwave heating of **1** efficiently generates acetylketene (**2**) which reacted *in situ* with a range of alcohols, aldehydes and trifluoroacetophenone, giving products in high isolated yields (Gudipati et al., 2008).



The synthesis of C6-cyclo secondary amine-substituted purine analogues in neat water was achieved with the aid of microwave irradiation, providing a rapid, efficient and convenient method for the preparation of acyclic nucleosides in high yields (Qu et al., 2008).

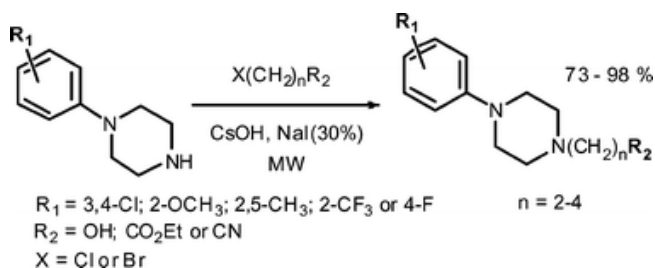


Microwave synthesis represents one of the important dimensions of modern chemistry. Microwave heating allows substantially improved productivity of many chemical processes with reduced formation of by-products caused by overheating. It offers a clean, cheap, and convenient method of heating which often results in higher yields and shorter reaction times. Also, due to its advantages of direct heating, high temperature homogeneity, reaction rate enhancement, as well as energy savings, microwave-assisted polymerization has become a fast-growing field of polymer research. In brief, microwave

referred as an effective eco-friendly organic synthesis reactions enhancement (EL-Malt, 2008).

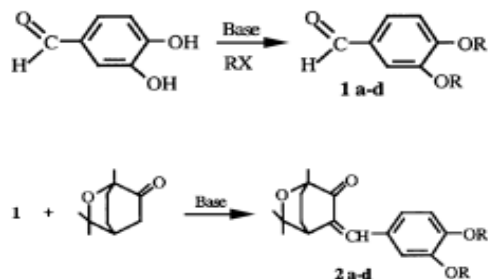
Solvent-free microwave-activation, in the liquid phase using an alumina supported V-Sb-O catalyst, affords highly efficient conversion (47%) of glycerol into acrylonitrile under mild conditions, short reaction times and in the absence of any solvent; in addition, it increases selectivity (>80%) compared to conventional thermal activation (Casilda *et al.*, 2009).

A series of some arylalkylpiperazines was prepared in good yields under microwave irradiation in dry media conditions using CsOH with high chemo- and regioselectivity (Giuglio-Tonolo *et al.*, 2009).



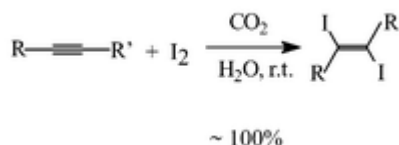
2.6.3. UV:

Microwave activation coupled with solvent-free phase transfer catalysis (PTC), as a green chemistry procedure, was applied to the synthesis of new benzylidene cineole derivatives as potential UVA filters. Considerable improvements over classical procedures are put into evidence when using KOH + K₂CO₃ as the base and TBAB as the phase transfer agent. Comparison with conventional heating in strictly the same conditions as under microwave revealed an important specific non-thermal microwave effect. Preliminary studies to evaluate the photochemical behaviour of these new derivatives were carried out (Villa *et al.*, 2001).

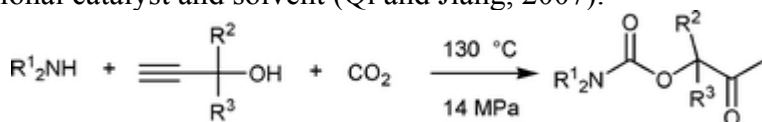


7.3. CO₂:

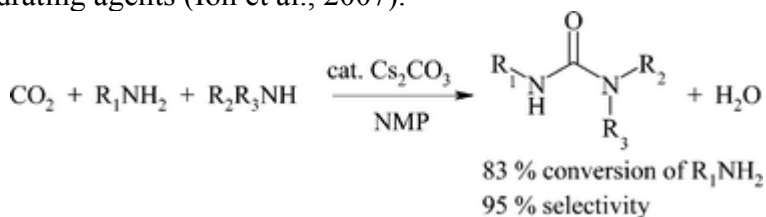
CO₂ is reported here as a Lewis assisted Brnsted acid accelerator to promote diiodination of alkynes. In the presence of CO₂, quantitative yields of trans-1,2-diiodoalkenes were obtained by diiodination of both electron-rich and electron-deficient alkynes with I₂ in H₂O (Li et al., 2002).



The efficient synthesis of β-oxopropylcarbamates *via* a three-component coupling of CO₂, secondary amines and propargyl alcohols was achieved in compressed carbon dioxide in the absence of any additional catalyst and solvent (Qi and Jiang, 2007).

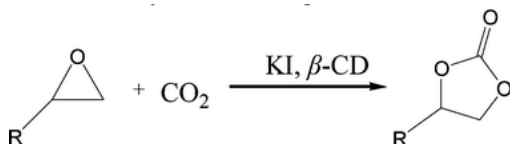


Using Cs⁺ base catalysts and *N*-methylpyrrolidone as the solvent, both symmetrical and asymmetrical urea derivatives are prepared in good yields directly from CO₂ and amines, in the absence of any dehydrating agents (Ion et al., 2007).

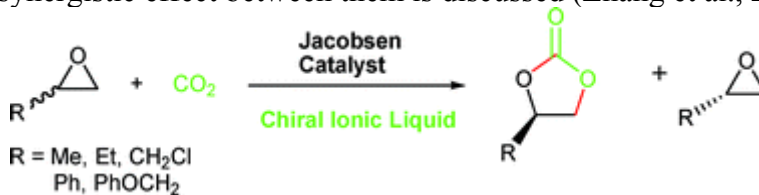


The synthesis of disubstituted ureas from amines and CO₂ were carried out using a basic ionic liquid (IL) 1-*n*-butyl-3-methyl imidazolium hydroxide ([Bmim]OH) as the catalyst. The results indicated that aliphatic amines, cyclohexylamine, and benzylamine could be converted to the corresponding ureas selectively in moderate yields under solvent-free conditions without using any dehydrating reagent. The IL could be reused after a simple separation procedure (Jiang *et al.*, 2008).

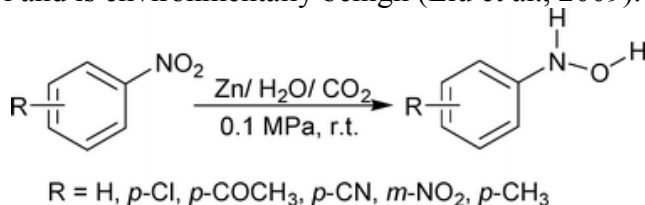
Cycloaddition of CO₂ with propylene oxide (PO) to propylene carbonate (PC) catalyzed by potassium halide (KCl, KBr, and KI) in the presence of β-cyclodextrin was studied at various conditions. It was discovered that potassium halide and β-cyclodextrin (β-CD) showed excellent synergetic effect in promoting the reactions, and KI-β-CD catalytic system was the most efficient among them (Song *et al.*, 2008).



The new catalyst system of chiral SalenCo(OAc)/chiral ionic liquid was developed to catalyze the asymmetric cycloaddition reaction of CO₂ and epoxides yielding the chiral cyclic carbonates. The synergistic effect between them is discussed (Zhang *et al.*, 2009).



Nitroarenes are reduced to the corresponding *N*-arylhydroxylamines with high selectivity using Zn dust in a CO₂/H₂O system under mild conditions. The process fully removes the need to use NH₄Cl and is environmentally benign (Liu *et al.*, 2009).



8.3. Ionic liquid:

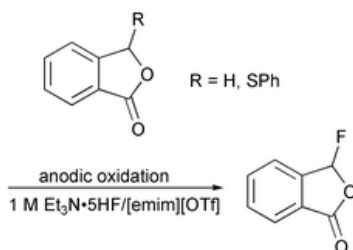
It has been demonstrated that enantioselective electrophilic fluorination performed by means of *N*-fluorocinchonium salts in ionic liquids presents substantial advantages over the use of classical solvents (Baudequin *et al.*, 2002).

A simple method for the N-alkylation of primary amines was developed using ionic liquids as solvent in order to prepare secondary amines selectively (Chiappe and Pieraccini, 2003).

The *O*-acetylation of alcohols with acetic anhydride to the corresponding esters has been achieved in excellent isolated yields in short reaction time at ambient conditions under ultrasonic irradiation in the absence of any added catalyst using a room temperature ionic liquid as the medium as well as a promoter for the reaction (Gholap *et al.*, 2003).

The application of ionic liquids as solvents for the enantioselective esterification of (*R,S*)-2-chloropropanoic acid with butan-1-ol using *Candida rugosa* lipase was reported by Gubicza *et al.* (2003).

Hasegawa *et al.* (2003) reported the anodic fluorination of phthalide and its derivatives by using $\text{Et}_4\text{NF}\cdot 4\text{HF}$, $\text{Et}_3\text{N}\cdot 5\text{HF}$ and imidazolium ionic liquids like 1-ethyl-3-methylimidazolium triflate [emim][OTf].



9.3. H_2O :

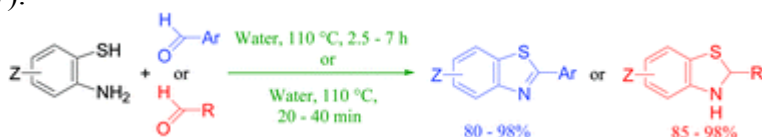
Dimethyl carbonate (DMC)–water is an environmentally benign solvent system for ruthenium tetraoxide oxidations of various substrates including alkenes, alkynes, arenes, alcohols, ethers and aldehydes. Either hydrated ruthenium trichloride or hydrated ruthenium dioxide can be used as sources of ruthenium, while suitable cooxidants include sodium periodate, bleach and Oxone[®] (Cornely *et al.*, 2003).

Water is an inexpensive and nontoxic reaction medium for the microwave-promoted Suzuki cross coupling of arylboronic acids with aryl halides. This environmentally friendly microwave protocol offers convenient operation and synthesis of a variety of substituted biaryls in good yield very rapidly employing $\text{PdCl}_2(\text{PPh}_3)_2$ as catalyst and potassium carbonate as the base (Bai *et al.*, 2003).

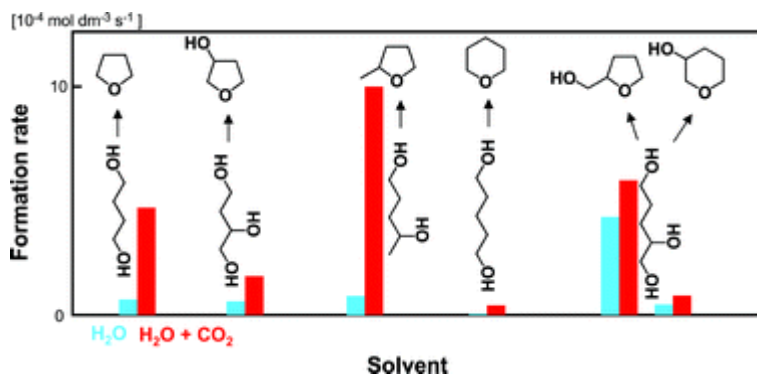
Amberlite[®] IR-120 Plus resin, a readily regenerated acidic solid resin, mediates the formation of tetrahydropyranol derivatives in water. Various aldehydes were reacted with homoallyl alcohol under the reaction conditions to yield the desired tetrahydropyranol derivatives in moderate to good yields (Keh and Li, 2003).

Optically active Diels–Alder adducts were prepared using a one-pot preparative method and enantioselective Diels–Alder reaction with optically active hosts in a water suspension medium (Miyamoto *et al.*, 2003).

A convenient and clean “on water”-mediated synthesis of benzothiazoles/ benzothiazolines is reported by Chakraborti *et al.* (2007).



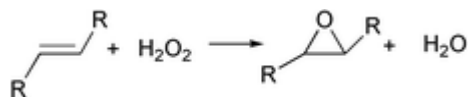
Cyclic ethers were produced by a dehydration reaction of polyalcohol compounds in high temperature liquid water, which was accelerated by the presence of carbon dioxide dissolved in the water. 3-hydroxytetrahydrofuran was produced by the dehydration of 1,2,4-butanetriol. Both tetrahydrofurfuryl alcohol and 3-hydroxytetrahydropyran were produced by the dehydration of 1,2,5-pentanetriol. Five-membered cyclic ethers were formed faster than six-membered cyclic ethers and the formation rates of the cyclic ethers depended strongly on the structure of the polyalcohol compounds. The position of the hydroxyl groups is crucial for the efficient intramolecular dehydration (Yamaguchi *et al.*, 2009).



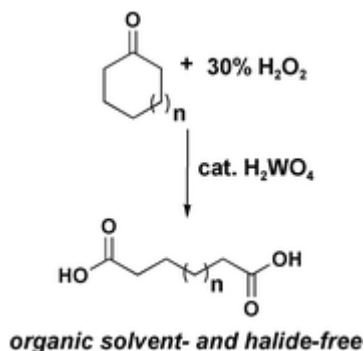
10.3. H₂O₂:

Hydrogen peroxide is a 'green' oxidant whose relatively high cost has prevented it from being applied to commodity chemical processing.

The epoxidation of alkenes using hydrogen peroxide as an environmentally friendly oxidant was reported by Grigoropoulou et al., (2003).

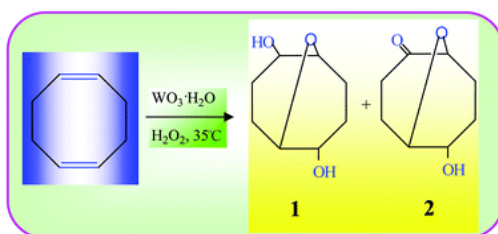


Cyclohexanone and cyclohexanol are oxidized to adipic acid in high yield with aqueous 30% H₂O₂ in the presence of H₂WO₄ as a catalyst under organic solvent- and halide-free conditions (Usui and Sato, 2003).

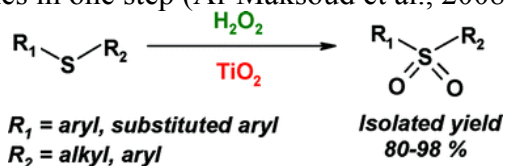


A carbon supported palladium catalyst (Pd/C) is successfully used in selective hydrogenation of α,β -unsaturated aldehydes in scCO₂ and under solventless reaction (Zhao *et al.*, 2003a).

The hydroxy- and carbonyl-derivatives of 9-oxabicyclo[3.3.1]nonane have been synthesized through an economic and green catalytic reaction between cycloocta-1,5-diene (COD) and aqueous H₂O₂ with tungstic acid as the catalyst. This process has advantages from the viewpoint of green chemistry, in that the aqueous H₂O₂ is used as the green oxygen donor, the only by-product of H₂O₂ is water and the tungstic acid catalyst can also be easily recovered. The excellent yields of the object products (1 and 2) (see Scheme 1) are reached easily under mild reaction conditions (Gao *et al.*, 2007).



The oxidation of thianisole and other substituted arylalkyl and diaryl sulfides with aqueous H_2O_2 as the oxidant and heterogeneous TiO_2 catalyst exhibits a high selectivity affording the corresponding sulfones with 80–98% isolated yields. The use of hydrogen peroxide and heterogeneous nanocrystalline titania catalyst is a green alternative to the traditional stoichiometric oxidation providing high yields of sulfones in one step (Al-Maksoud *et al.*, 2008).

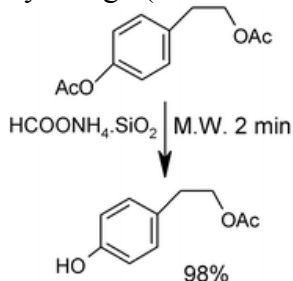


11.3. Silica:

Morpholinated and 8-hydroxyquinolinated silica gel were obtained via reaction of silica chloride with morpholine and 8-hydroxyquinoline, respectively, as reported by Zolfigol *et al.* (2002).

Conjugate addition of both linear and cyclic α -nitro ketones to conjugated enones, can be efficiently performed under heterogeneous, solvent-free and mild acidic conditions, by silica (Ballini *et al.*, 2003).

Several aryl acetates were rapidly and selectively deprotected to the corresponding phenols in excellent yields using silica gel supported ammonium formate under microwave irradiation. The process is environmentally benign (Ramesh *et al.*, 2003).

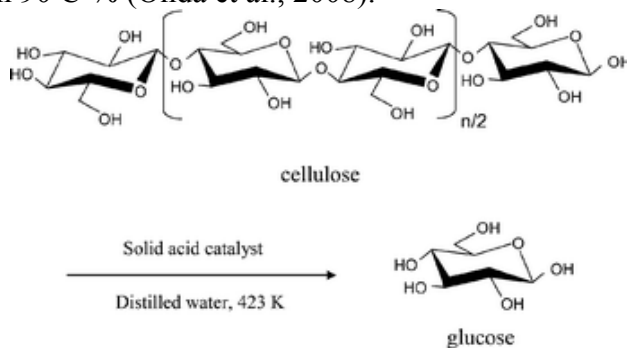


12.3. Solid catalysis:

The synthesis of 2-methyl-2-naphthyl-4-methyl-1,3-dioxolane, a compound with blossom orange scent, has been successfully carried out by acetalization reaction between methyl naphthyl ketone and propylene glycol using different acid solid catalysts (Climent et al., 2002).

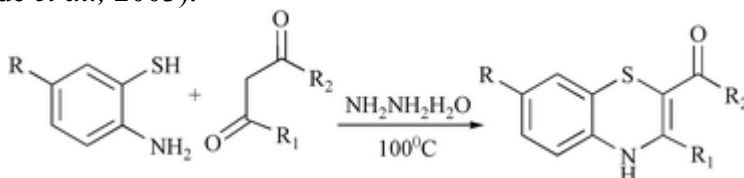
Novel environmentally benign solid-state brominations of anilines and phenols with gaseous bromine and solid bromination reagents are described. In most cases the reactions proceeded in the absence of solvents with higher yields and selectivities than in solution (Toda and Schmeyers, 2003).

The mildly hydrothermal method using solid acid catalysts for the glucose production from cellulose can be one of the key technologies for a future sustainable society using cellulose biomass. This article is the first to indicate solid acid catalysis for the hydrolysis of cellulose with β -1,4-glycosidic bonds into glucose selectively higher than 90 C-% (Onda et al., 2008).

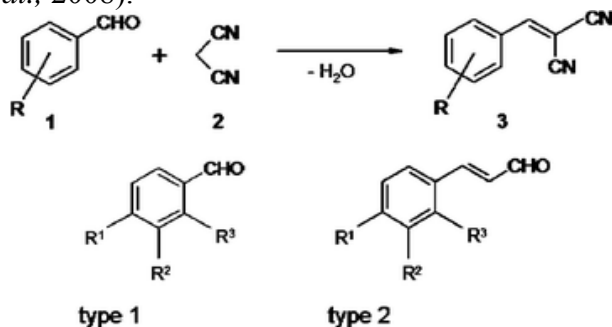


13.3. Solvent-free:

A rapid, solvent free synthetic strategy for the oxidative cyclocondensation of 2-aminobenzenethiols and 1,3-dicarbonyls using a catalytic amount of hydrazine hydrate has been developed in order to obtain 2,3-disubstituted-1,4-benzothiazines in high yields (83–96%) (Munde *et al.*, 2003).

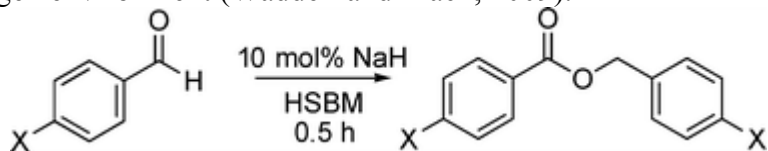


The mechanochemical reaction of malononitrile with various aldehydes was studied with the goal to achieve quantitative stoichiometric conversion of the reactants to their corresponding benzylidene-malononitriles in absence of any solvents and catalysts (Trotzki *et al.*, 2008).

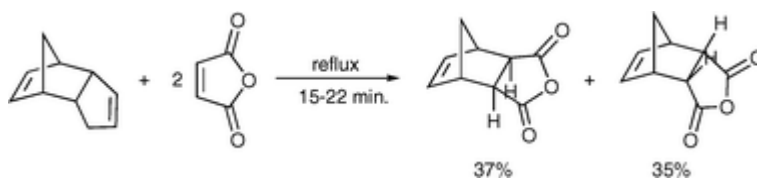


The reaction selectivities of acid catalyzed ring opening reactions of epoxidized methyl oleate (methyl-9,10-epoxy stearate; EMO), to form either ketal (acetal) or branched ester products have been reported by Doll and Erhan (2008).

Herein, we describe the solvent-free ball milling Tishchenko reaction. Using high speed ball milling and a sodium hydride catalyst, the Tishchenko reaction was performed for aryl aldehydes in high yields in 0.5 hours. The reaction is not affected by the type of ball bearing used and can be successful when conducted in a liquid nitrogen environment (Waddell and Mack, 2009).



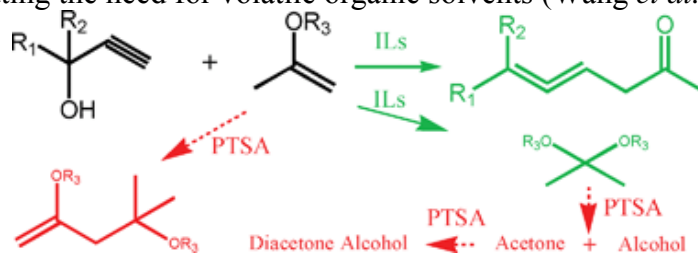
A solvent-free Diels–Alder reaction was carried out by heating a mixture of dicyclopentadiene and a dienophile. Cyclopentadiene, formed *in situ*, reacted with the dienophile in a thermodynamically controlled reaction. Besides being solvent-free, the described procedure allows for almost complete utilization of dicyclopentadiene and avoids handling of noxious and hazardous cyclopentadiene (Huertas *et al.*, 2009).



A series of some arylalkylpiperazines was prepared by Tonolo *et al.* (2009) in good yields under microwave irradiation in dry media conditions using CsOH with high chemo- and regioselectivity.



Simple ammonium ionic liquids are efficient catalysts in promoting Saucy–Marbet reactions of unsaturated alcohols with unsaturated ethers to afford the corresponding unsaturated ketones, eliminating the need for volatile organic solvents (Wang *et al.*, 2009).



It is clear that, the rules of the green chemistry will not be enough to prevent our environment; it is time to search an effective strategy to save our world.

REFERENCES

- Al-Maksoud, W.; Daniele, S. and Sorokin, A. (2008): Practical oxidation of sulfides to sulfones by H_2O_2 catalysed by titanium catalyst. *Green Chem.*, 10: 447 – 451.

- Bai, L.; Wang, J. and Zhang, Y. (2003): Rapid microwave-promoted Suzuki cross coupling reaction in water. *Green Chem.*, 2003, 5 (5), 615 – 617.
- Balakrishnan, M.; Batra, V.; Hargreaves, J.; Monaghan, A.; Pulford, I.; Rico, J. and Sushil, S. (2009): Hydrogen production from methane in the presence of red mud –*making mud magnetic*. *Green Chem.*, 11: 42 – 47.
- Ballini, R.; Fiorini, D.; Gil, M. and Palmieri, A. (2003): Michael addition of α -nitro ketones to conjugated enones under solventless conditions using silica. *Green Chem.*, 2003, 5 (4), 475 – 476.
- Ballivet-Tkatchenko, D.; Picquet, M.; Solinas, M.; Franci, G.; Wasserscheid, P. and Leitner, W. (2003): Acrylate dimerisation under ionic liquid–supercritical carbon dioxide conditions. *Green Chem.*, 2003, 5 (2), 232 – 235.
- Baudequin, C.; Plaquevent, J.; Audouard, C. and Cahard, D. (2002): Enantioselective electrophilic fluorination in ionic liquids. *Green Chem.*, 2002, 4 (6), 584 - 586
- Beckers, J.; Gaudillère, C.; Farrusseng, D. and Rothenberg, G. (2009): Marrying gas power and hydrogen energy: A catalytic system for combining methane conversion and hydrogen generation. Article citation: Jurriaan Beckers, *Green Chem.*, 2009, DOI: 10.1039/b900516a
- Bruckmann, A.; Krebs, A. and Bolm, C. (2008): Organocatalytic reactions: effects of ball milling, microwave and ultrasound irradiation. *Green Chem.*, 2008, 10, 1131 - 1141, DOI: 10.1039/b812536h
- Capello, C.; Fischer, U. and Hungerbühler, K. (2007): What is a green solvent? A comprehensive framework for the environmental assessment of solvents. *Green Chem.*, 9: 927 – 934.
- Casilda, V.; Pérez, M. and Bañares, M. (2009): Efficient microwave-promoted acrylonitrile sustainable synthesis from glycerol. *Green Chem.*, 11: 475 - 483
- Chakraborti, A.; Rudrawar, S.; Jadhav, K.; Kaur, G. and Chankeshwara, S. (2007): "On water" organic synthesis: a highly efficient and clean synthesis of 2-aryl/heteroaryl/styryl

- benzothiazoles and 2-alkyl/aryl alkyl benzothiazolines. *Green Chem.*, 2007, 9, 1335 – 1340.
- Chiappe,C. and Pieraccini,D. (2003): Direct mono-N-alkylation of amines in ionic liquids: chemoselectivity and reactivity. *Green Chem.*, 2003, 5 (2), 193 – 197.
- Climont,M.J. A.Velty and A.Corma (2002): Design of a solid catalyst for the synthesis of a molecule with blossom orange scent. *Green Chem.*, 2002, 4 (6), 565 - 569
- Cornely,J.; Ham,L.; Meade,D. and Dragojlovic,V. (2003): Dimethyl carbonate–water: an environmentally friendly solvent system for ruthenium tetraoxide oxidations. *Green Chem.*, 2003, 5 (1), 34 – 37.
- Dandia,A.; Sati,M. and Loupy,A. (2002): Dry-media one-pot syntheses of fluorinated-2,3-dihydro-1,5-benzothiazepines under microwave activation. *Green Chem.*, 2002, 4 (6), 599 - 602
- Danks,T.N. and Desai,B. (2002): Alumina-supported formate for the hydrogenation of alkenes. *Green Chem.*, 2002, 4 (2), 179 - 180 .
- Doll,K. and Erhan,S. (2008): Synthesis of cyclic acetals (ketals) from oleochemicals using a solvent free method. *Green Chem.*, 10: 712 – 717.
- EL-Malt, E.A. (2008): Green chemistry: Microwave-Assisted eco-friendly organic compounds synthesis. *Egypt. Agric. Res.*, 86(3): 939-950.
- Foreman,M.; Ekberg,C. and Jensen,A. (2008): Hydrogenation catalysts from used nickel metal hydride batteries. *Green Chem.*, 2008, 10, 825 – 826.
- Gao,R.; Dai,W.; Le,Y.; Yang,X.; Cao,Y.; Li,H. and Fan,K. (2007): A green process for *O*-heterocyclization of cycloocta-1,5-diene by peroxotungstic species with aqueous H₂O₂. *Green Chem.*, 2007, 9, 878 – 881.
- Gellis,A.; Boufatah,N. and Vanelle,P. (2006): Rapid microwave-promoted synthesis of new sulfonylmethylbenzothiazoles in water. *Green Chem.*, 2006, 8, 483 – 487.
- Gholap,A.; Venkatesan,K.; Daniel,T.; Lahoti,R. and Srinivasan,K. (2003): Ultrasound promoted acetylation of alcohols in room

- temperature ionic liquid under ambient conditions. *Green Chem.*, 2003, 5, (Advance Article).
- Giuglio-Tonolo,A.; Terme,T. and Vanelle,P. (2009): Solventless microwave assisted protocol for synthesis of arylalkylpiperazines using Cs-base. *Green Chem.*, 2009,11: 160 – 162.
- Grigoropoulou;G.; Clark,J.H. and Elings,J.A. (2003): Recent developments on the epoxidation of alkenes using hydrogen peroxide as an oxidant. *Green Chem.*, 2003, 5, (Advance Article)
- Gubicza,L.; Nemestthy,N.; Frter,T. and Bélafi-Bak,K. (2003): Enzymatic esterification in ionic liquids integrated with pervaporation for water removal. *Green Chem.*, 2003, 5 (2), 236 – 239.
- Gudipati,I. Sadasivam,D. and Birney,D. (2008): Microwave generation and trapping of acetylketene. *Green Chem.*, 2008,10: 275 – 277.
- Hasegawa,M.; Ishii,H. and Fuchigami,T. (2003): Selective anodic fluorination of phthalides in ionic liquids. *Green Chem.*, 2003, 5 (5), 512 – 515.
- Huertas,D.; Florscher,M. and Dragojlovic,V. (2009): Solvent-free Diels–Alder reactions of *in situ* generated cyclopentadiene. *Green Chem.*, 2009,11, 91 – 95.
- Ion,A.; Parvulescu,V.; Jacobs,P. and Vos,D. (2007): Synthesis of symmetrical or asymmetrical urea compounds from CO₂ via base catalysis. *Green Chem.*, 9: 158 – 161.
- Jiang,T.; Ma,X.; Zhou,Y.; Liang,S.; Zhang,J. and Han,B. (2008): Solvent-free synthesis of substituted ureas from CO₂ and amines with a functional ionic liquid as the catalyst. *Green Chem.*, 2008, 10, 465 – 469.
- K.Keh,C.C. and Li,C.J. (2003): Direct formation of 2,4-disubstituted tetrahydropyrans in water mediated by an acidic solid resin. *Green Chem.*, 2003, 5,(Advance Article).
- Kabalka,G.W.; Pagni,R.M.; Wang,L.; Namboodiri,V. and Hair,C.M. (2000): Microwave-assisted, solventless Suzuki coupling reactions on palladium-doped alumina. *Green Chem.*, 2000, 2 (3), 120 – 122.
- Lancaster, M. (2000): Green chemistry. *Education in Chem.*, March,40-43.

- Li, J.H.; Xie, Y.X. and Yin, D.L. (2002): New role of carbon dioxide in Lewis assisted Bronsted acid accelerated diiodination of alkynes in water. *Green Chem.*, 2002, 4 (5), 505 - 506
- Liu, S.; Wang, Y.; Jiang, J. and Jin, Z. (2009): The selective reduction of nitroarenes to *N*-arylhydroxylamines using Zn in a CO₂/H₂O system. *Green Chem.*, 2009, DOI: 10.1039/b906283a
- Lopez-Pestaña, J.M. , Vila-Rey, M.J. and Martzn-Aranda, R.M. (2002): Ultrasound-promoted *N*-alkylation of imidazole. Catalysis by solid-base, alkali-metal doped carbons. *Green Chem.*, 2002, 4 (6), 628 - 630
- Miyamoto, H.; Kimura, T.; Daikawa, N. and Tanaka, K. (2003): Preparation of optically active *cis*-4-methylcyclohex-4-ene-1,2-dicarboximides by a combination of Diels–Alder reaction and complexation with optically active hosts and enantioselective Diels–Alder reaction in inclusion crystals in a water suspension medium. *Green Chem.*, 2003, 5, (Advance Article)
- Munde, S.; Bondge, S.; Bhingolikar, V. and Mane, R. (2003): A facile synthesis of 1,4-benzothiazines under solvent free conditions. *Green Chem.*, 2003, 5 (2), 278 – 279.
- Namoodiri, V.V. and Varma, R.S. (2001): Microwave-accelerated Suzuki cross-coupling reaction in polyethylene glycol (PEG). *Green Chem.*, 2001, 3 (3), 146 – 148
- Okkerse, C. and H. Van Berkkum (1999): From fossil to Green. *Green Chem.*, 1(2):107-114.
- Onda, A.; Ochi, T. and Yanagisawa, K. (2008): Selective hydrolysis of cellulose into glucose over solid acid catalysts. *Green Chem.*, 2008, 10, 1033 - 1037, DOI: 10.1039/b808471h
- Peng, Y. and Song, G. (2003): Combined microwave and ultrasound accelerated Knoevenagel–Doebner reaction in aqueous media: a green route to 3-aryl acrylic acids. *Green Chem.*, 2003, 5, (Advance Article).
- Peng, Y.; Song, G. and Dou, R. (2006): Surface cleaning under combined microwave and ultrasound irradiation: flash synthesis of 4*H*-pyrano[2,3-*c*]pyrazoles in aqueous media. *Green Chem.*, 2006, 8, 573 - 575, DOI: 10.1039/b601209d

- Qi,C. and Jiang,H. (2007): Efficient synthesis of β -oxopropylcarbamates in compressed CO₂ without any additional catalyst and solvent. *Green Chem.*, 2007, 9, 1284 – 1286.
- Qu,G. Lin Zhao,L. Dong-Chao Wang, Jing Wu and Hai-Ming Guo (2008): Microwave-promoted efficient synthesis of C6-cyclo secondary amine substituted purine analogues in neat water. *Green Chem.*, 10: 287 – 289.
- Ramesh,C.; Mahender,G.; Ravindranath,N. and Das,B. (2003): A convenient, rapid, highly selective and eco-friendly method for deprotection of aryl acetates using silica gel supported ammonium formate under microwave irradiation. *Green Chem.*, 2003, 5 (1), 68 – 70.
- Ranu,B.; Dey,S. and Hajra,A. (2003): Highly efficient acylation of alcohols, amines and thiols under solvent-free and catalyst-free conditions. *Green Chem.*, 2003, 5 (1), 44 – 46.
- Reid,M.; Clark,J. and Macquarrie,D. (2006): Solventless microwave-assisted chlorodehydroxylation for the conversion of alcohols to alkyl chlorides. *Green Chem.*, 8: 437 – 438.
- Song,J.; Zhang,Z.; Han,B.; Hu,S.; Li,W. and Xie,Y. (2008): Synthesis of cyclic carbonates from epoxides and CO₂ catalyzed by potassium halide in the presence of β -cyclodextrin. *Green Chem.*, 2008, 10, 1337 – 1341.
- Takenaka,Y.; Kiyosu,T; Choi,J.; Sakakura,T. and Yasuda,H. (2008): Selective synthesis of *N*-aryl hydroxylamines by the hydrogenation of nitroaromatics using supported platinum catalysts. *Green Chem.*, 10: 825 – 826.
- Toda,F. and Schmeyers,J. (2003): Selective solid-state brominations of anilines and phenols. *Green Chem.*, 2003, 5, (Advance Article).
- Tonolo,A.; Terme,T. and Vanelle,P. (2009): Solventless microwave assisted protocol for synthesis of arylalkylpiperazines using Cs-base. *Green Chem.*, 11: 160 – 162.
- Trotzki,R.; Hoffmann,M. and Ondruschka,B. (2008): Studies on the solvent-free and waste-free Knoevenagel condensation. *Green Chem.*, 10: 767 – 772.

- Usui, Y. and Sato, K. (2003): A green method of adipic acid synthesis: organic solvent- and halide-free oxidation of cycloalkanones with 30% hydrogen peroxide. *Green Chem.*, 2003, 5 (4), 373 – 375.
- Verdugo, E.; Liu, Z.; Ramirez, E.; Garcia, J.; Dubreuil, J.; Hyde, J.; Hamley, P. and Poliakoff, M. (2006): *In situ* generation of hydrogen for continuous hydrogenation reactions in high temperature water. *Green Chem.*, 8: 359 – 364.
- Villa, C.; M. T. Genta, A. Bargagna, E. Mariani and A. Loupy (2001): Microwave activation and solvent-free phase transfer catalysis for the synthesis of new benzylidene cineole derivatives as potential UV sunscreens. *Green Chem.*, 3(4): 196 - 200
- Villa, C.; Mariani, E.; Loupy, A.; Grippo, C.; Grossi, G. and Bargagna, A. (2003): Solvent-free reactions as green chemistry procedures for the synthesis of cosmetic fatty esters. *Green Chem.*, 5 (5): 623-626.
- Villemin, D.; Jullien, A. and Bar, N. (2003): Optimisation of solvent free parallel synthesis under microwave irradiation: synthesis of new arylacrylonitriles. *Green Chem.*, 5 (4): 467-469.
- Waddell, D. and Mack, J. (2009): An environmentally benign solvent-free Tishchenko reaction. *Green Chem.*, 11: 79-82.
- Wang, C.; Zhao, W.; Li, H. and Guo, L. (2009): Solvent-free synthesis of unsaturated ketones by the Saucy–Marbet reaction using simple ammonium ionic liquid as a catalyst. *Green Chem.*, 11: 843-847.
- Yamaguchi, A.; Hiyoshi, N.; Sato, O.; Bando, K. and Shirai, M. (2009): Enhancement of cyclic ether formation from polyalcohol compounds in high temperature liquid water by high pressure carbon dioxide. *Green Chem.*, 11: 48-52.
- Zhang, L.; Luo, Y.; Fan, R. and Wu, J. (2007): Metal- and solvent-free conditions for the acylation reaction catalyzed by carbon tetrabromide (CBr₄). *Green Chem.*, 9: 1022-1025.
- Zhang, S.; Huang, Y.; Jing, H.; Yao, W. and Yan, P. (2009): Chiral ionic liquids improved the asymmetric cycloaddition of CO₂ to epoxides. Article citation: Suling Zhang, *Green Chem.*, 2009, DOI: 10.1039/b821513h

Zhao, F.; Ikushima, Y. and Arai, M. (2003): Hydrogenation of 2-butyne-1,4-diol to butane-1,4-diol in supercritical carbon dioxide. *Green Chem.*, 5 (5): 656-658.

Zhao, F.; Ikushima, Y.; Chatterjee, M.; Shirai, M. and Arai, M. (2003a): An effective and recyclable catalyst for hydrogenation of α,β -unsaturated aldehydes into saturated aldehydes in supercritical carbon dioxide. *Green Chem.*, 5 (1): 76-79.

Zolfigol, M.A.; Tayyeb Madrakian, Ezat Ghaemi, Abbas Afkhami, Saeid Azizian and Shahrara Afshar (2002): Synthesis of morpholinated and 8-hydroxyquinolinated silica gel and their application to water softening. *Green Chem.*, 4 (6): 611-614.

الكيمياء العضوية الخضراء

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قسم الكيمياء الزراعية – كلية الزراعة – جامعة المنيا

إن كارثة التلوث هي مشكلة رئيسية في كافة أنحاء العالم وهي لها أثر غير مناسب على حياة ملايين من الناس من خلال العديد من اضطرابات الصحة والوفيات. المادة الملوثة هي تلك المادة التي عند وجودها في البيئة، تسمم الهواء والأرض والماء. والمواد الكيماوية سمّت كلّ العالم، وأحدثت أذى للبشر، والحياة البرية، وحياة نبات، وعلى الأرض وفي البحر والهواء. حوالي مائة ألف مادة كيماوية صناعية الآن في السوق، مع تقريبا ألف مادة كيماوية جديدة إضافية سنويا. بالرغم من أن الشركات المنتجة للكيماويات تختبر سمية منتجاتهم بشكل منفرد، فتلك المواد لن توجد بمفردها في البيئة. وسوف تنتج مركبات معدلة جديدة بالتمزاج مع المركبات الأخرى، وتأثير هذه المجموعات لم تختبر أو تدرس. مبيدات الحشرات، صمّم لقتل الحشرات والأعشاب الضارة والفطر، وهي سامة أيضا إلى الأنظمة العصبية للإنسان. كلّ مادة كيماوية نستعمل، كلّ مادة كيماوية عضوية ننتجها أو نصنعها في مجال الزراعة مثلا تبقى على الأرض. فهي لا تختفي في الحقيقة بل تختبئ فقط. المنتجات الكيماوية.

الكيمياء العضوية الخضراء هي فلسفة و طريقة تفكير. وهي ليس فرع جديد من الكيمياء ولكن هي استخدام مجموعة من الأدوات والتكنولوجيات والتقنيات التي يمكن أن تساعد الكيميائيين في إنتاج وتطوير منتجات ودية بيئية وأكثر كفاءة. وتهتم الكيمياء العضوية الخضراء باستخدام مجموعة المبادئ التي يمكن أن تخفض أو تزيل إستعمال المواد الخطرة في تصميم، وصناعة وتطبيق المركبات الكيماوية. وكذلك تهدف لإستبدال المواد الكاشفة الخطرة بأخرى قابلة للتجديد وأكثر أمانا؛ وكذلك تقليل أو إزالة النواتج الثانوية للفاعلات وتفادي استخدام مواد مساعدة، مثل المذيبات والكواشف المساعدة بقدر الإمكان.

في فترة قليلة، من الواضح أنّ، قواعد الكيمياء الخضراء لن تكون بما فيه الكفاية أن تمنع البيئة؛ لقد حان الوقت لتفتيش عن إستراتيجية فعالة أكثر أو إستراتيجية أخرى مصاحبة لتوفير الأمان لعالمنا.