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GREEN CHEMISTRY: SOLVENTLESS AS A NEW APPROACH FOR A GREENER ORGANIC CHEMICAL REACTIONS

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ABSTRACT

The term "green chemistry," describes an area of research and chemical practice that arises from scientific discoveries about pollution and ecological interdependence. Green chemistry is not necessarily environmental chemistry, although it may involve some of this. It is chemistry for the environment. Green chemistry tries to avoid pollution by utilizing green processes. One of the twelve principles of green chemistry asks us to: 'use safer solvents and auxiliaries'.

The expansion of solvent-free organic synthetic methods has thus become an important and popular research area. Reports on solvent-free reactions between solids, between gases and solids, between solids and liquid, between liquids, and on solid inorganic supports have become increasingly frequent in recent years. The avoiding of organic solvents in organic syntheses is a most important goal in green chemistry. Solvent-free organic reactions make syntheses much simpler, save energy, and prevent solvent wastes, hazards, and toxicity.

What is Green Chemistry?

Green chemistry is an approach to the design, manufacture and use of chemical products to intentionally reduce or eliminate chemical hazards (Clark and Macquarrie, 2002). The goal of green chemistry is to create better, safer chemicals while choosing the safest, most efficient ways to synthesize them and to reduce wastes. The twelve principles of green chemistry asked us to use safer solvents (Anastas and Warner, 1998).

The green chemistry is chemistry which is environmentally eco-friendly. One obvious way for chemistry to be green is to use solventless reaction conditions, instead of toxic organic solvents.

What is a solvent?

The solvent is a liquid, solid, or gas that dissolves another solid, liquid, or gaseous solute, resulting in a solution that is soluble in a certain volume of solvent at a specified temperature.

Advantages and Disadvantages of solvents :

The use of solvents had some advantages and disadvantages. There advantages include some important points like to: It can be used to Place reagents into a common phase where they can react, Dissolve solids so they can be pumped from place to place, Lower viscosity and facilitate mixing, Regulate temperatures of reactions by heating at reflux, Moderate the vigor of exothermic reactions, Allow recovery of solids by filtration or centrifugation, Extract compounds from mixtures, Purify compounds by recrystallization, Remove azeotrope compounds from reactions, Clean equipment and clothing and Place a thin film of material on to a substrate.

The disadvantages of solvents include the following: Loss of 10–15 million tons of solvents (with a fuel value of 2 billion dollars) each year, Reaction of lost solvents in air with nitrogen oxides in sunlight to produce ground level ozone, Destruction of upper atmosphere ozone by chlorofluorocarbons, Toxicity of chlorinated and other solvents to workers, Miscarriages caused by ethers of ethylene glycol, Birth defects from exposure to solvents, Fires and explosions may result from use and Monetary cost. (Anastas, 1996; Anastas and Farris, 1994; Hancock and Cavanaugh, 1994).

Solventless reaction (it is also called, dry media reaction or solid-state reaction) is a chemical reaction system in the absence of a solvent. The drive for the development of solventless reactions in chemistry is economics (save money on solvents) ease of purification (no solvent removal post-synthesis) high reaction rate (due to high concentration of reactants) environmentally friendly (solvent is not required).

In many cases, organic reactions can not be carried out without solvents. If possible, the use of solvents should be avoided, or if they cannot be eliminated, we should try to use innocuous substances

instead. In some cases, particularly in the manufacture of bulk chemicals, it is possible to use solventless conditions.

Yet in most cases, including specialty and pharmaceutical products, a solvent is required to assist in processing and transporting of materials. Alternative solvents suitable for green chemistry are those that have low toxicity, are easy to recycle, are inert and do not contaminate the product.

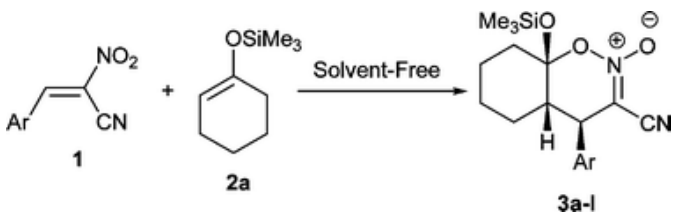
Traditional chemical synthesis focused on optimizing yields, with little regard to a chemical's impact on the environment and its long term viability. There is now a realization that more benign chemical synthesis is required, as an integral part of developing sustainable technologies. Reducing the use of organic solvents can minimize the generation of waste, which is a requirement of one of the principles of green chemistry

There is no perfect green solvent that can apply to all situations and therefore decisions have to be made. However, we must first consider the uses, hazards and properties of solvents in general.

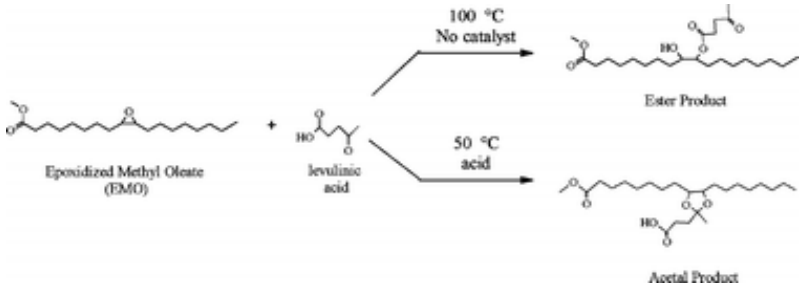
Solvent-free as a greener organic synthesis reactions:

Commercially available ISOLUTE® Si-carbonate catalyzes both nitroaldol and Michael reactions, from nitroalkanes and under solvent-free conditions, yielding nitroalkanols and γ-nitro-functionalized carbonyl and cyano derivatives (Ballini *et al.*, 2008).

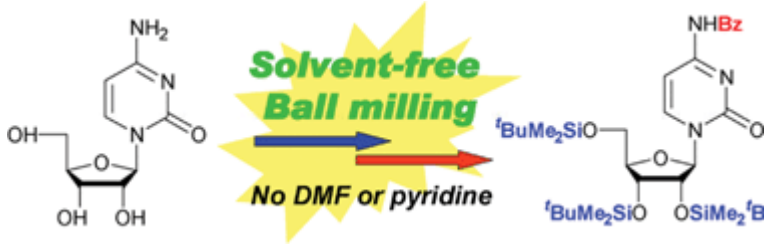
Under solvent-free conditions, (*E*)-2-aryl-1-cyano-1-nitroethenes 1a–l rapidly react with 1-(trimethylsilyloxy)-cyclohex-1-ene (2a) leading to the exclusive formation of the *cis*-fused hexahydro-*4H*-benzoxazine-2-oxides 3a–l (Bellachioma *et al.*, 2008).



Selective production of ketal or ester type surfactant precursors starting from soybean based methyl oleate (Doll *et al.*, 2008).

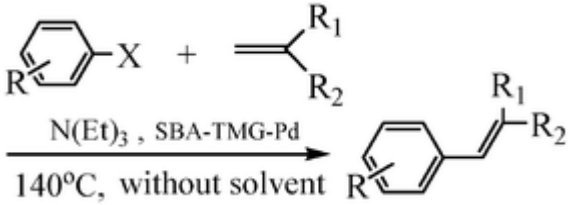


Undesirable solvents such as DMF and pyridine are avoided by using solvent-free ball milling. Reactions are fast, quantitative and potentially applicable to many other biological molecules with difficult solubility profiles (Giri *et al.*, 2008).



The organic product methyl-(*Z*)-α-acetamido cinnamate can be crystallized from the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate by either using a shift to lower temperatures or by using a shift to higher carbon dioxide concentrations (Kroon *et al.*, 2008).

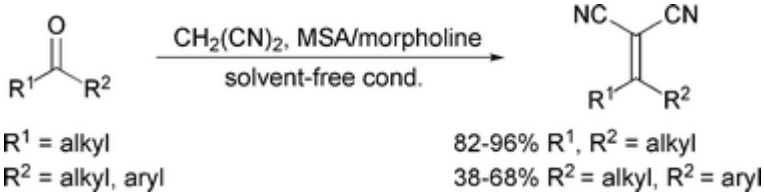
The Pd catalyst supported on 1,1,3,3-tetramethylguanidinium (TMG)-modified molecular sieve SBA-15 is a very active and stable catalyst for the Heck coupling reaction in solvent-free conditions. It is easy to separate the supported catalyst from the reaction mixture and reuse it (Ma *et al.,* 2008).



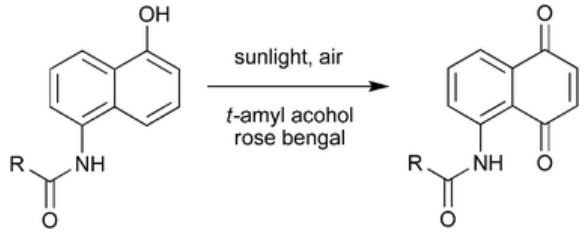
Ethyl lactate is characterized both from micro and macroscopic viewpoints in wide pressure/temperature ranges using several experimental and theoretical approaches. Competing intra and intermolecular hydrogen bonding are characterized leading to the molecular level organization and macroscopic properties (Aparicio and Alcalde, 2009).

The epoxidation of cyclooctene under solvent-free conditions gives high activity with high epoxide selectivity using graphite-supported gold nanoparticles prepared using a sol-immobilisation method (Bawaked *et al.*, 2009).

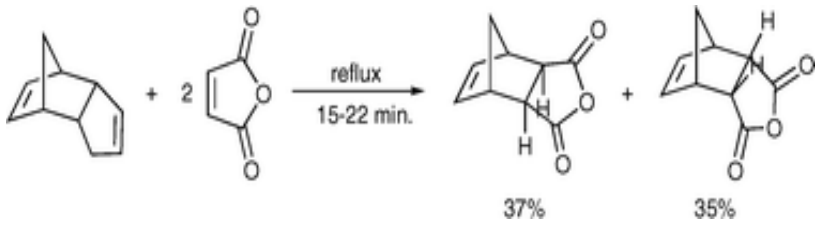
The new, alternative and greener route for Knoevenagel condensations of ketones with malononitrile without the need for organic solvents is described (Góra *et al.*, 2009).



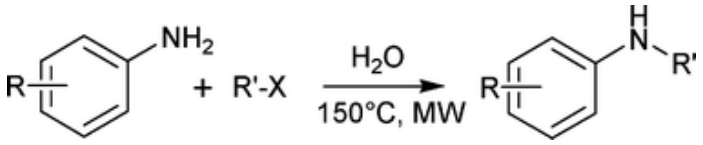
Dye sensitized photooxygenations of 5-amido-1-naphthols gave the corresponding 5-amido-1,4-naphthoquinones in moderate to excellent yields. The solar process gave higher yields in almost all cases studied and allowed for significant energy savings (Haggiage *et al.*, 2009).



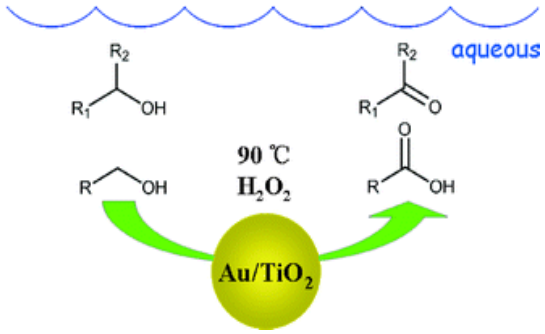
Dicyclopentadiene was used as a source of *in situ* generated cyclopentadiene for Diels–Alder reactions under solvent-free conditions (Huertas *et al.*, 2009).



A greener improvement to direct mono-*N*-alkylation of aromatic amines by alkyl halides was achieved using microwave irradiation in water without any catalyst (Marzaro *et al.*, 2009).

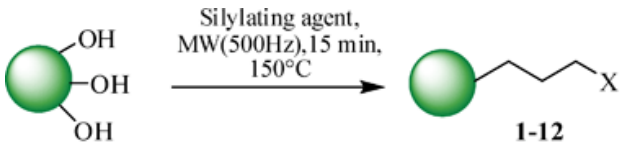


The use of supported gold nanoparticles as an efficient, green and reusable catalyst for the oxidation of various alcohols to the corresponding carbonyl compounds using aqueous hydrogen peroxide as an environmentally benign oxidant is presented (Ni *et al.*, 2009).



An efficient, solvent-free, catalyst-free process for the generation of strong, conducting, paramagnetic carbon spheres by the thermal degradation of waste polyethylene terephthalate polymer [PET] under autogenic pressure is demonstrated (Pol *et al.*, 2009).

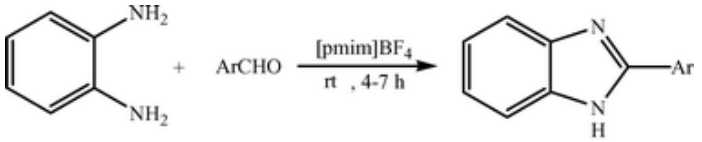
A fast and versatile MW-assisted method for the post-calcination functionalization of MCM-41 is proposed. The efficiency of the grafting is improved in the absence of solvent and depends on the MW-heating time (Procopio *et al.*, 2009).



1-12

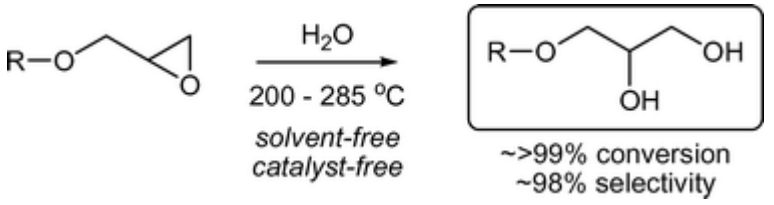
X= SH, NH_2; Cl, $(CH_3)_2$; CN; NCO; $(CH_2)_4CH_3$; 
$NH(CH_2)_2NH_2$; Ph; $[NH(CH_2)_2]_2NH_2$; $NHC(O)NH_2$.

An easily accessible ionic liquid, $[pmim]BF_4$ efficiently catalyzes the condensation of *o*-phenylenediamine and aromatic aldehydes at room temperature in open air to produce a variety of structurally diverse 2-arylbenzimidazoles avoiding use of any hazardous organic solvent (Saha *et al.*, 2009).

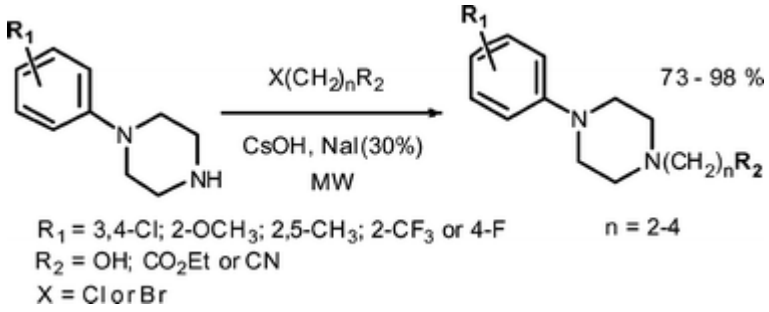


80 - 94 %

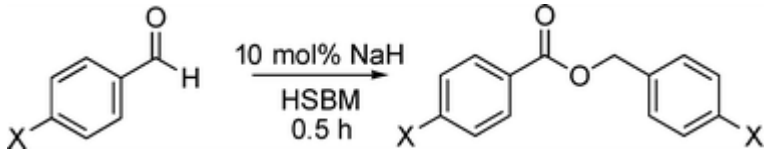
Hydrolysis of hydrophobic glycidyl ethers in pressurized water media afforded the corresponding glycidyl ethers in good to excellent selectivity within several minutes without catalyst (Saito *et al.*, 2009).



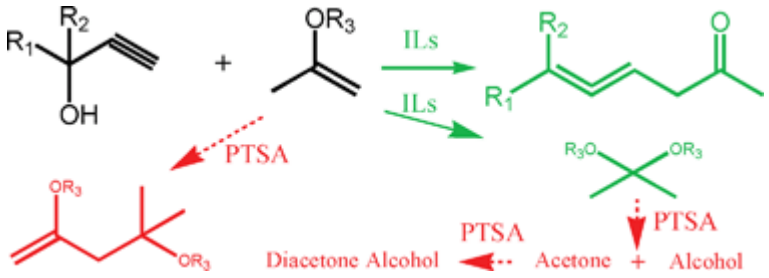
A series of some arylalkylpiperazines was prepared in good yields under microwave irradiation in dry media conditions using CsOH (Tonolo *et al.*, 2009).



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).

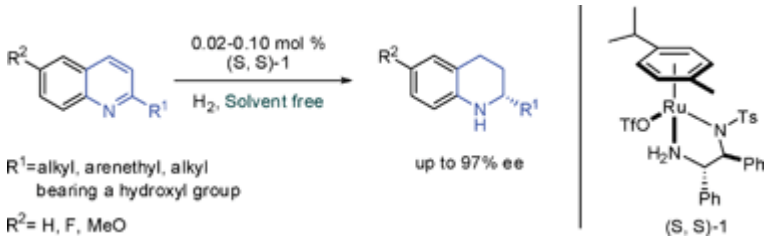


Simple ammonium ionic liquids are used as highly efficient catalysts for Saucy–Marbet reactions to synthesize unsaturated ketones from unsaturated alcohols and unsaturated ethers, eliminating the need for volatile organic solvents (Wang *et al.*, 2009).

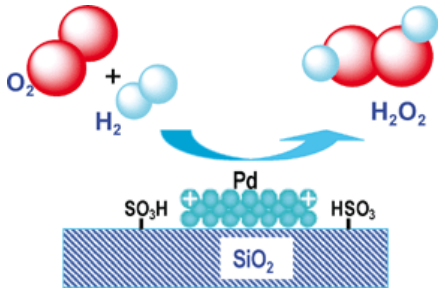


The phosphine-free chiral cationic Ru(OTf) (TsDPEN) (η^6-cymene) complex was found to be an efficient catalyst for the enantioselective hydrogenation of quinolines under more environmentally friendly solvent-free or highly concentrated

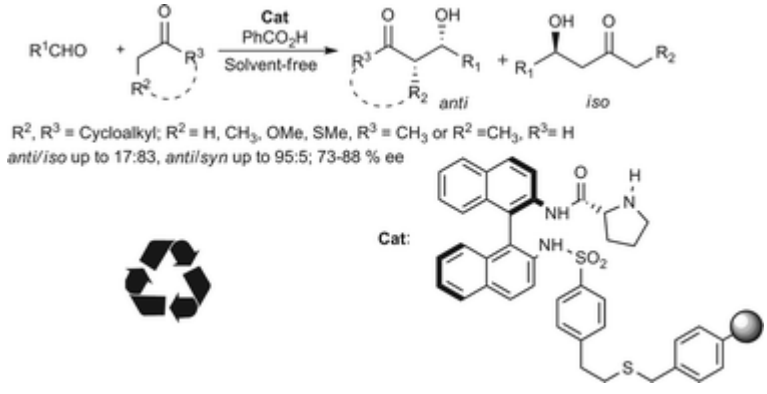
conditions with excellent yields and high enantioselectivities (up to 97% ee) at only 0.02–0.10 mol% catalyst loading (Wang *et al.*, 2009).



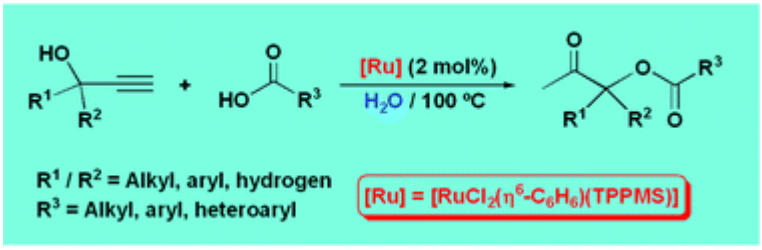
Direct synthesis of H_2O_2 has been successfully achieved at high-concentration and high selectivity at realistic reaction temperatures (313 K) on Pd-loaded sulfonic acid-functionalized silica using non-acidic solutions (Brieva *et al.*, 2010).



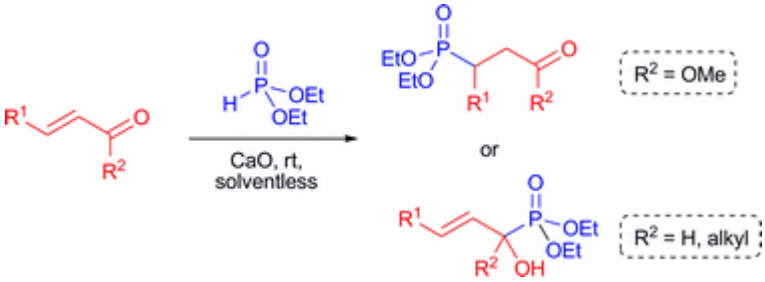
Polystyrene-supported *N*-sulfonyl-(R_a)-binam-D-prolinamide was used as an efficient catalyst for the enantioselective direct aldol reaction under solvent-free or aqueous conditions, with catalyst recovery and reuse being possible (Caballero *et al.*, 2010).



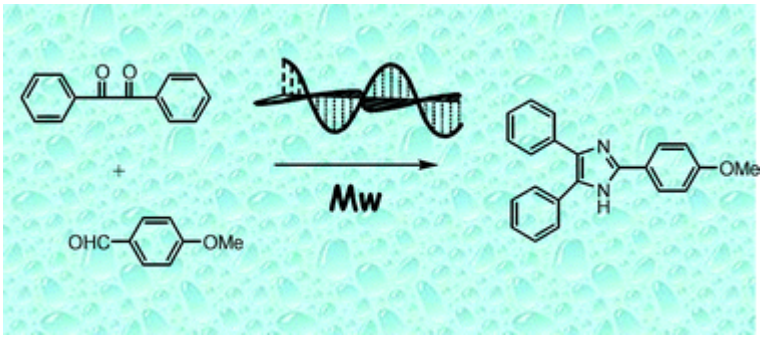
Selective synthesis of β-oxo esters, by addition of carboxylic acids to terminal propargylic alcohols, can be efficiently performed in water using hydrosoluble ruthenium(II) catalysts (Cadierno *et al.*, 2010).



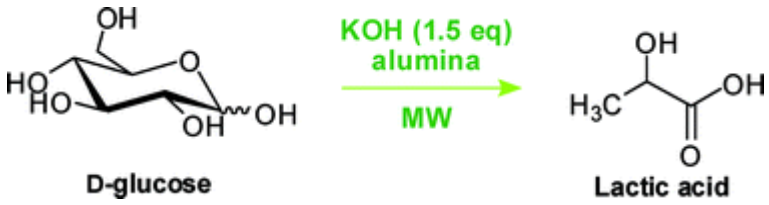
Regioselectivity in the CaO-promoted nucleophilic addition of diethyl phosphite to α,β-unsaturated systems follows a definite trend depending on the nature of the substituent on carbonyl (Castro *et al.*, 2010).



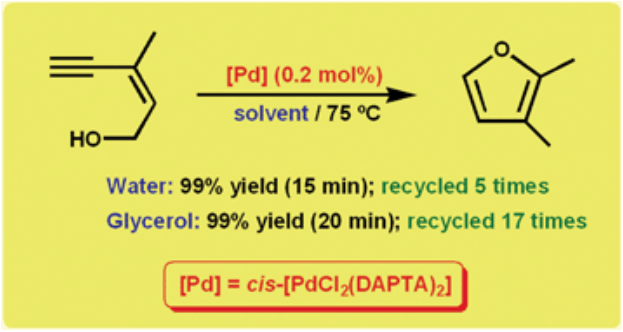
A series of 2,4,5-triarylimidazoles was synthesized from a new, highly efficient and green method. The reaction is performed in water, without the presence of any catalyst, and under microwave irradiation (Chauveau *et al.*, 2010).



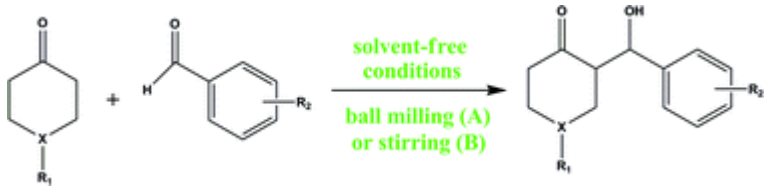
Efficient conversion of D-glucose into lactic acid is described using microwave irradiation in solventless condition with alumina supported potassium hydroxide (Epane *et al.*, 2010).



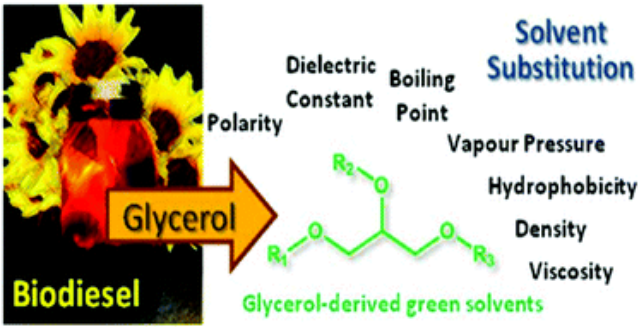
Palladium-catalyzed heteroannulation reactions of (*Z*)-2-en-4-yn-1-ol derivatives into furans have been studied using water and glycerol as alternative green reaction media. Higher activities were observed in water, but catalyst recycling was much more effective in glycerol (Francos and Cadierno, 2010).



Molecular topology has been used to achieve mathematical models capable of predicting the yields and the reaction times of different reactions under solvent-free conditions. The results have implications for the efficacy of the methodology employed in helping experimentalists to achieve greener and more sustainable reactants and products (Gálvez *et al.*, 2010).

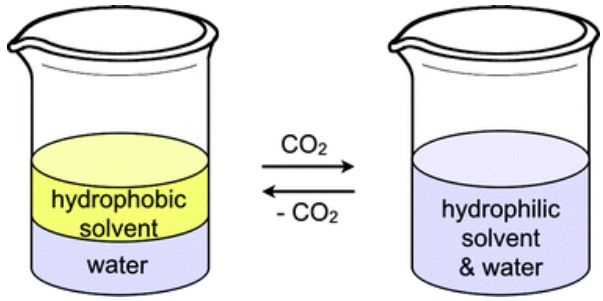


62 glycerol derivatives, 1,3-dialkoxy-2-propanols and 1,2,3-trialkoxypropanes, have been synthesized and their possible role as substitutive solvents has been evaluated through measurements of their physico-chemical properties (García *et al.*, 2010).

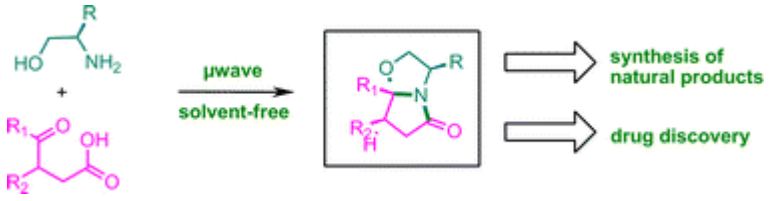


Glycerol, an organic waste generated by the biodiesel industry, has been recently proposed as a valuable green solvent. This review summarizes the advantages, disadvantages and potential uses of glycerol as a green solvent for catalysis, organic synthesis, separations and materials chemistry. In particular, through selected examples we show here that glycerol may combine the advantages of water (low toxicity, low price, large availability, renewability) and ionic liquids (high boiling point, low vapour pressure, low solubility in $scCO_2$). More generally, all these reported works contribute to increase the portfolio of available green solvents and afford innovative solutions to the substitution of the conventionally used volatile organic solvents (Gu and Jérôme, 2010).

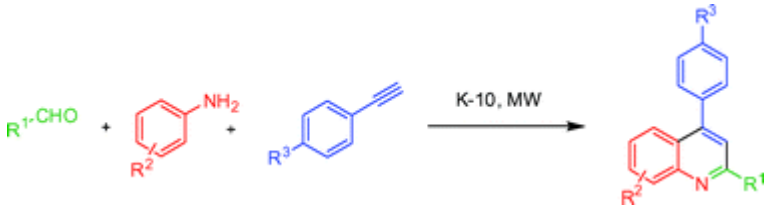
A switchable-hydrophilicity solvent is a liquid solvent that normally has very poor miscibility with water, but when exposed to 1 bar of CO_2 becomes miscible with water (Jessop *et al.*, 2010).



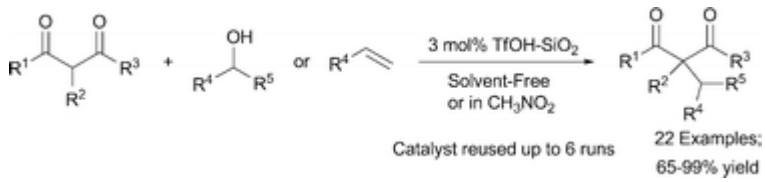
Solvent-free microwave-activation allows the efficient synthesis of bicyclic or tricyclic lactams *via* the Meyers' reaction in excellent yields and good diastereoselectivities in very short times. This is the first greener alternative for this reaction that is a keystone for syntheses of natural products derivatives and bioactive compounds in drug discovery (Jida *et al.*, 2010).



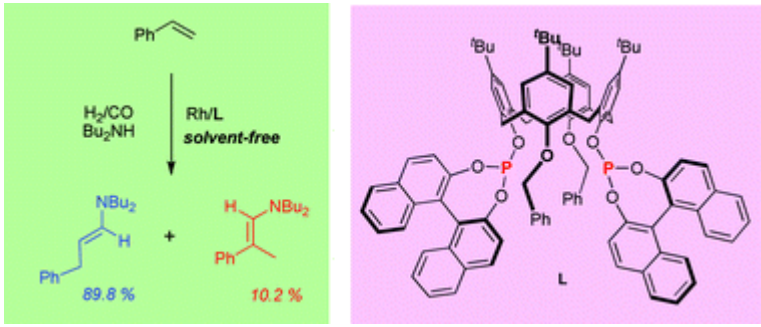
A solid, acid-catalyzed, microwave-assisted multicomponent domino reaction of anilines, aldehydes and terminal aryl alkynes yields quinolines with nearly 90% atom economy in excellent yields in a matter of minutes (Kulkarni and Török, 2010).



The readily available triflic acid supported on silica gel was applied as an efficient and recyclable catalyst for the heterogeneous addition of β-dicarbonyl compounds to alcohols and alkenes, which afforded moderate to excellent yields under solvent-free conditions or in nitromethane (Liu *et al.*, 2010).

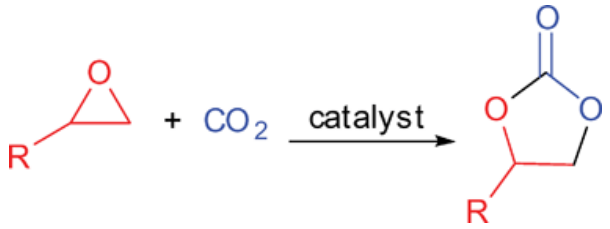


Selective, one-pot hydroaminovinylation was achieved under *solvent-free* conditions with rhodium complexes based on hemispherical diphosphite ligands (Monnereau *et al.*, 2010).



A synthesis of indolizines, which had been previously reported to proceed with metal catalysts, has been shown to proceed with water alone or in polar protic solvents (Narayan and Sarpong, 2010).

The synthesis of cyclic carbonates from epoxides and CO_2 is reviewed with emphasis on the green credentials of the reaction (North *et al.*, 2010).

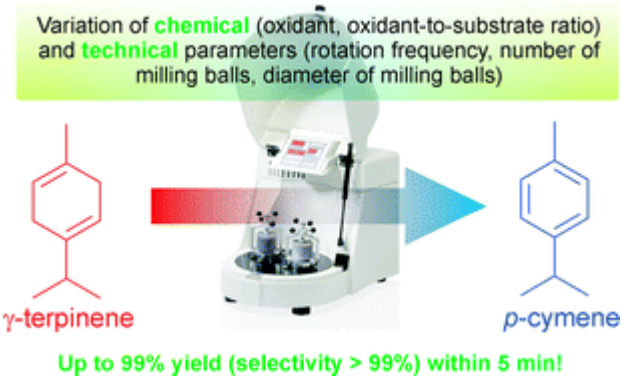


Renewable dicarboxylic acids are soluble in methanol-modified carbon dioxide, whereas levulinic acid and 3-hydroxybutryolactone are soluble in neat carbon dioxide (Payne and Kerton, 2010).

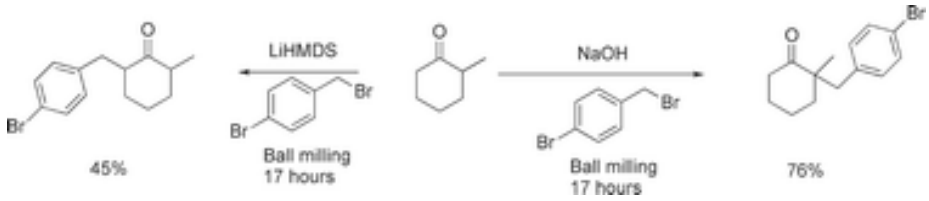
We report an eco-friendly synthesis of selenoesters from acyl chlorides catalyzed by recyclable CuO nanopowder in ionic liquid as a recyclable solvent in good to excellent yields. This protocol shows high efficiency in catalyzing this transformation in a greener fashion. (Singh *et al.*, 2010)

Carbon nanotube supported Pt nanocatalysts have an unprecedented activity and selectivity for the hydrogenation of nitrobenzene to aniline in the absence of solvent under mild conditions (Sun *et al.*, 2010).

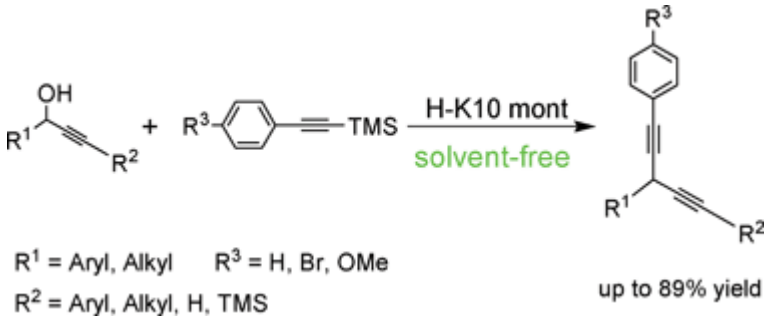
A solvent-free dehydrogenation reaction in a ball mill is used to assess chemical and technical variables for this reaction model. Experiments revealed that $KMnO_4$ can be replaced by less hazardous oxidants ($NaIO_4$, Oxone®), retaining excellent selectivity (Szuppa *et al.*, 2010).



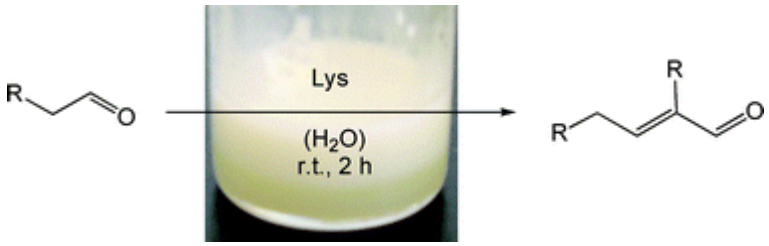
An investigation of the ability to selectively form products arising from a kinetic or a thermodynamic enolate under solvent-free high speed ball milling conditions (Waddell *et al.*, 2010).



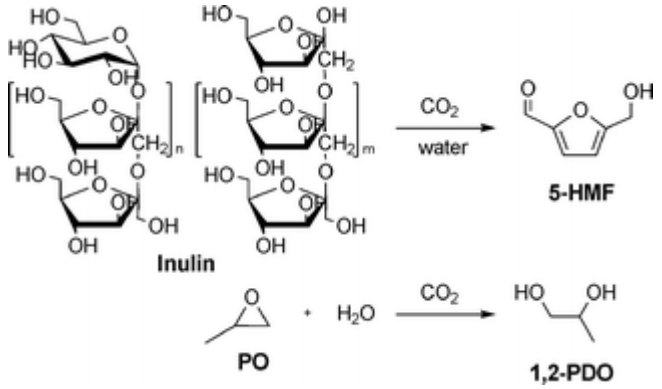
A solvent-free solid acid-catalyzed nucleophilic substitution of propargylic alcohols with alkynylsilanes is described (Wang *et al.*, 2010).



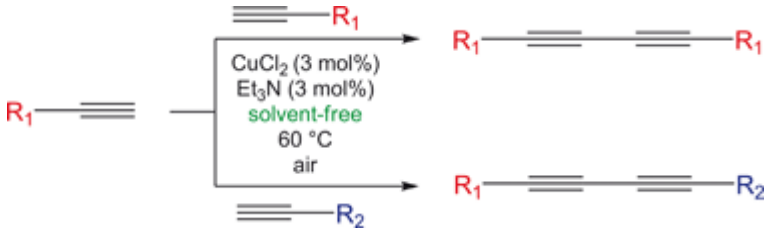
A self-condensation of aldehydes has been conveniently accomplished by the catalytic action of lysine in water or a solvent-free system under specific emulsion. This process is applicable to various aldehydes, especially to long-chain aldehydes (Watanabe *et al.*, 2010).



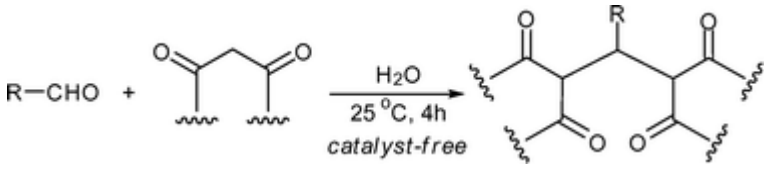
CO_2 can enhance the conversion of inulin to 5-hydroxymethylfurfural (5-HMF) and of propylene oxide (PO) to 1,2-propanediol (1,2-PDO) in water (Wu *et al.*, 2010).



An environmentally friendly, efficient method for transforming terminal acetylenes into 1,3-diynes based on catalytic amounts of a Cu(II) salt and base under solvent-free conditions is developed; in addition, the catalyst can be recycled (Wang *et al.*, 2010).



A greener improvement to the synthesis of tetraketones by the Knoevenagel condensation and Michael addition between aldehydes and cyclic-1,3-diketones was achieved using water as the solvent without catalyst (Yu *et al.*, 2010).



It is satisfaction to say that the world attention towards the green chemistry increased day after day. Reports on solvent-free reactions between solids, between gases and solids, between solids and liquid, between liquids, and on solid inorganic supports have become increasingly frequent in recent years.

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الكيمياء الخضراء: تفاعلات اللامذيبات كطريق جديد نحو تفاعلات كيميائية عضوية أكثر خضرة

أ.د/ عصام أحمد الملط

قسم الكيمياء الزراعية – كلية الزراعة – جامعة المنيا

مصطلح الكيمياء الخضراء، يصف الأبحاث والممارسات الكيميائية التى تنشأ نتيجة للإكتشافات العلمية المتعلقة بالتلوث وحماية البيئة. الكيمياء الخضراء ليست كيمياء بيئية بالضرورة، بالرغم من أنّ بعض مفاهيمها تتضمن أهداف الكيمياء البيئية. تحاول الكيمياء الخضراء تفادي التلوث بإستعمال العمليات الخضراء. أحد أهم المبادئ الإثنى عشر للكيمياء الخضراء تنص على : ' إستعمال مذيبات أكثر أمانا '.

التوسّع فى طرق التخليق العضوية الخالية من المذيبات هو مجال العديد من الدراسات والأبحاث الحالية. هناك العديد من الدراسات على التفاعلات الخالية من المذيبات فى الطرق المستخدمة للتفاعلات بين المواد الصلبة وبعضها، بين الغازات والمواد الصلبة، بين المواد الصلبة والسائل، بين السوائل وبعضها، والمواد غير العضوية الصلبة، وتنامى الاهتمام بها كثيراً في السنوات الأخيرة.

إنّ تفادي إستخدام المذيبات عضوي في التفاعلات العضوية هو هدف من أكثر الأهداف أهمية في الكيمياء الخضراء. تفاعلات اللامذيبات فى الكيمياء العضوية تجعل طرق التخليق أكثر سهولة وتوفيراً للطاقة، وتمنع نفايات المذيبات وتكون الماد السامة والخطرة.