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Solventless substitution chemistry of iron and ruthenium metal carbonyl complexes

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2008-03-06T10:24:52Z
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CHAPTER 2: GREEN CHEMISTRY

2.1. Genesis of Green Chemistry

Chemistry has played a central role in the improvement of human life especially during the last two centuries. Different domains have benefited from chemistry research and dramatic revolutions have taken place from these findings.

At the time when antibiotics were still unknown, diseases ravaged mankind. If one became ill, a disease could easily spread in a population potentially leading to the extinction of life, but with the invention of antibiotics, many diseases have become curable. In general, the medical revolution has arisen from developments in chemistry research which has raised the average life expectancy from 47 in 1900 to 75 years in the 1990s[1].

With the production of chemicals that protect and enhance crops growth (fertilizers, pesticides) by the chemical industry, food security has been reached in many countries and the problem of hunger has been satisfactorily solved. Nowadays, chickens can be raised for consumption in few weeks instead of months as was the case traditionally due to the progress in food chemistry [2, 3].

People are not much influenced by weather conditions because of the success in the textile industry which uses synthetic fibres [4, 5].

We can see the impact of chemistry in our daily lives: without products from petroleum such as gasoline and diesel or their homologues, it could be not be possible to drive a car; to perform a surgery a doctor needs an anaesthetic, detergents are very useful in cleaning objects; to print documents from a computer or photocopier, a toner is needed. These are just a few examples to illustrate the important position chemistry has in the modern society.

From the above considerations, one could expect everybody in this world to be enjoying the advantages brought about by chemistry innovation and to have a high regard for chemists.

In contrast, many members of the society see chemistry and chemicals in a different light. For them, chemicals are something to be afraid of, and to be avoided as much as possible.

So where does this negative consideration, this tarnished image of chemistry come from, in spite of all the achievements realized by chemistry?

One of the answers to this question could be that, notwithstanding, the unbelievable achievements of chemistry, at the same time, there has been a high cost to pay in terms of human health and the environment. A few examples can be used to clarify this statement:

Everyone knows how pesticides are very efficient in improving crop growth. In 1962, Rachael Carson reported how the use of DDT and other pesticides could spread throughout the food chain causing irreparable and unanticipated harm to the environment [6, 7, 8].
A substance called "Thalidomide" ($C_{13}H_{10}N_2O_4$) has been used by pregnant women to reduce the effects of nausea and vomiting during pregnancy. Unfortunately, it was later discovered that children born to mothers taking this drug suffered acute birth defects in the form of missing or grossly deformed limbs [9, 10].

The contamination of Times Beach soil by the toxic dioxin from dioxin-tainted waste oil and the leak of toxic chemicals through a clay cap which was support to seal a garbage dump in Love canal in Niagara Falls NY are more recent examples of environmental contamination by chemicals [11].

In the 1980s it was discovered that the chlorofluorocarbons CFC's have a negative impact on the atmosphere by destroying the ozone layer resulting in global warming [12].

Accidental chemical disasters like in Bhopal, India, where methyl isocyanate killed hundreds of people and the eruption of toxic gases from Lake Nyos, Cameroon, can also be listed among catastrophes arising from the presence of chemicals [13].

Given this dilemma that chemistry is viewed on the one hand as beneficial to human society, and on the other hand, chemistry is seen as more harmful than beneficial, one obvious question can be asked:

Is it possible to do Chemistry by keeping its beneficial side and simultaneously eliminating or reducing its negative effects on human health and the environment?

To answer this question is to suggest that those manufacturing chemicals add another aspect to their systems so that when considering the production of a desired product, they consider also the short and long term effects, its degradation and disposal of chemical wastes.

Indeed recently, chemists have commenced a reconsideration of chemical production and this has led to the birth or genesis of what has been referred to as *Green chemistry* in the early 1990's.

As defined by P.T Anastas and J.C Warner [14], Green Chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of a chemical product.

In the green chemistry approach, the term hazard comprises all the types of dangers that are part of the production of a substance: explosiveness, flammability, corrodibility but also acute and chronic toxicity, carcinogenicity, ecological toxicity as well as global threats like global warming, resource depletion and persistence of chemicals in the environment.

The whole philosophy of Green chemistry relies on the fact that it is better to prevent that to cure. It is less dangerous and less costly to prevent the production of waste that to treat the waste after it has been produced.

Different terminologies such as environmentally benign chemical synthesis, alternative synthetic pathways for pollution prevention, benign by design etc. are currently used to convey the same message that it is better to prevent pollution than to treat hazardous substances once formed [14].

Green chemistry is governed by some principles which serve as guidelines to enhance human health and environmental protection.

2.2. Principles of green Chemistry [14, 15]

1. It is better to prevent waste than to treat or clean up waste after it is formed.

Design reactions that do not generate waste, the need for separation, treatment and disposal of hazardous substances will be eliminated automatically.

2. Synthetic methods should be designed to maximize the incorporation of all materials used into the final product.

Do not judge the success of a reaction by the yield of the desired product formed but take into account the quantity and nature of by-products generated by the reaction.

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.*

Do not rely on the exposure control methods because sometimes they can fail but reduce the intrinsic toxicity in order to minimize the risk.

4. *Chemical products should be designed to preserve efficacy of function while reducing toxicity.*

From the understanding of reaction mechanism and toxicology, design safer chemicals while maintaining the desired purpose of the product.

5. *The use of auxiliary substances (e.g. solvents, separation agents…) should be made unnecessary wherever possible and innocuous when used.*

Avoid as much as it is possible the use of auxiliary substances for they can become part of the waste stream and pose an environmental hazard.

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.*

Lower the energy required for a particular reaction whenever possible because it is a potential for environmental harm and carries an environmental cost.

7. *A raw material of feedstock should be renewable rather than depleting wherever technically practicable.*

Do not deplete natural reserves; look for alternative feedstock in order to develop sustainable chemical industry.

8. *Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.*

Do not pass by multi-step synthesis if really not necessary. The additional steps result in increase in materials, time and energy.

9. *Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.*

Drive the reaction to a preferred product by using a catalyst in order to reduce waste generation and energy needed for the reaction.

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.*

Give the fate of the chemical products a priority in the process design because the persistence of chemicals in the environment may pose a risk to organisms due to exposure and bioaccumulation.

11. *Analytical methodologies need to be developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.*

Incorporate in-line monitoring in your processes in order to maximize yield and minimize 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.*

Avoid chemical accidents as much as possible for they can have a devastating effect on a local community.

Inspired by the Green chemistry principles, numerous domains of chemistry are currently being revisited in order to comply with the ideas of cleaner chemistry.

2. 3. New chemistry methodologies based on the principles of Green Chemistry.

2.3.1. Solventless chemistry

2.3.1.1. Historical and generalities

Traditionally, chemical syntheses and transformations were carried out in solvents to facilitate the mass and heat transfer as well as the isolation and purification of the desired product from the reaction mixture [16, 17]. In some chemical reactions, the solvent was even used without any special reason simply because as said by Aristotle 'no coopora nisi fluida' meaning no reaction without solvent [18].

Nevertheless, those solvents are often volatile and hazardous for the human health and the environment.

As stipulated in principles 1 and 5 of the twelve principles of green chemistry, it is better to prevent the production of waste than to treat waste after it is formed and the use of unnecessary auxiliary substances like solvents should be avoided.

Therefore, new synthesis methodologies such as procedures carrying out chemical transformations in the absence of solvents are needed. A number of terminologies are currently used to refer to those procedures: solvent-free, solventless, solid-solid, solid state, dry medium reactions [19]. Hence, a modern chemist should minimize as much as possible the use of solvents in the chemical reaction design.

However, the chemical transformations in the absence of solvents were practised from long time ago. Historically, a solvent-free transformation can be recorded already from the prehistorical time when the primitive man was using friction to make fire [20] but it has been reported that the first written document about a solvent-free chemical reaction comes from Theophrastus (371-286 B.C) in his book 'De Lapidibus' (on stones) [21]. He noted that if a native cinnabar is rubbed in a brass mortar with a brass pestle in the presence of vinegar, metallic mercury is obtained. This phenomenon was described by the following chemical reaction:

$$HgS + Cu \longrightarrow Hg + CuS$$

After historical reviews, the chemical transformations in the absence of solvent reappeared in the end of 19th century with the work of Carey Lea [20, 22, 23] as well as the work of Ling and Baker in 1893 [24, 25]. The latter managed to prepare quinhydrone by only grinding two solids together. Seemingly this discovery did not attract much interest from researchers for more than a half century.

In 1960's, Rastogi and co-workers [26, 27, 28] conducted detailed investigations about fundamental issues governing the reaction between two solids such as mobility on the interface, kinetics and mechanism. In 1984, Patil et al [29] prepared successfully unsymetrically substituted quinhydrones.

The idea was to find an alternative way of obtaining these products because the solution procedure was problematic due to the self oxidation reactions that were observed. In 1987, Toda et al [24] introduced the idea of host-guest complex formation in the solid state. The mechanism proposed is that the quinine sublimes and its vapor attacks certain hydroquinone's sites.

In all these experiments, the procedure consisted in just grinding solid reactants together in agate mortar and pestle.

In general, two methods can be used to bring about a solventless chemical reaction: mechanochemical activation or thermochemical activation.

2.3.1.2. Mechanochemical activation

As defined by Ostwald [20, 30], 'mechanochemistry' is a branch of chemistry which deals with chemical and physico-chemical changes of substances in all states of aggregation'. In other words mechanochemistry consists in a mechanical mixing of chemical reagents to bring about the reaction at room temperature. A range of mills such as ball mill, planetary mill, vibratory mill, stirring ball mill, pin mill, rolling mill etc. can be used in mechanochemical activation [21].

Most of the historical solvent-free transformations were carried out using mechanochemical procedures. Nowadays, mechanochemistry is a well established in material sciences and solid state chemistry.

2.3.1.3. Thermochemical activation

There are chemical systems which do not lead to a chemical reaction by simply mixing the reagents at room temperature. They are pushed to react by rising the temperature and this results in most of cases in the formation of a melt phase, and then the reaction takes place in a melt phase. Rothenberg and co-workers [31] established that most of solvent-free reactions which were thought to occur in solid phase were really happening in the melt phase.

However, the melt phase formation is not a guarantee that necessarily a chemical reaction will take place [32]. It has been found that other factors such as reagent concentration, temperature, electronic and steric properties etc. determine significantly the rate and pathways of a solvent-free reaction.

Solvent free procedures present some advantages among others, no medium to collect and purify, compounds once formed are often pure, higher yields are normally obtained compared with procedures using solvents, no need for specialized equipment to carry out the reaction etc.[33]. The disadvantages related to the solvent-free procedures entail the formation of hot spots in the reaction medium that could lead to possibility of runaway reactions.

Generally, solventless reactions can be broadly classified into three main categories [18]:

- Reaction between neat reactants: solid/solid, solid/liquid, liquid/liquid, gas/solid
- Reaction between reactants supported on a solid mineral such as silica, alumina or clays

- Reactions carried out under phase transfer catalysis

Solventless reactions are currently applied in various fields of chemistry

2.3.1.4. Solventless reactions in organic chemistry

Organic chemistry was the first field to reveal a large number of applications of the solventless procedures in chemical synthesis [34]. Many systems which were previously conducted in organic solvents can now be done in solventless media. Some examples are listed below:

McCluskey et al [35] have demonstrated that the Koevenagel condensation reaction between substituted benzaldehydes and cyanoamides in the presence of piperidine as a catalyst proceeded faster and led to higher yields in solvent-free conditions compared with refluxing ethanol or refluxing water conditions (figure 2.1).

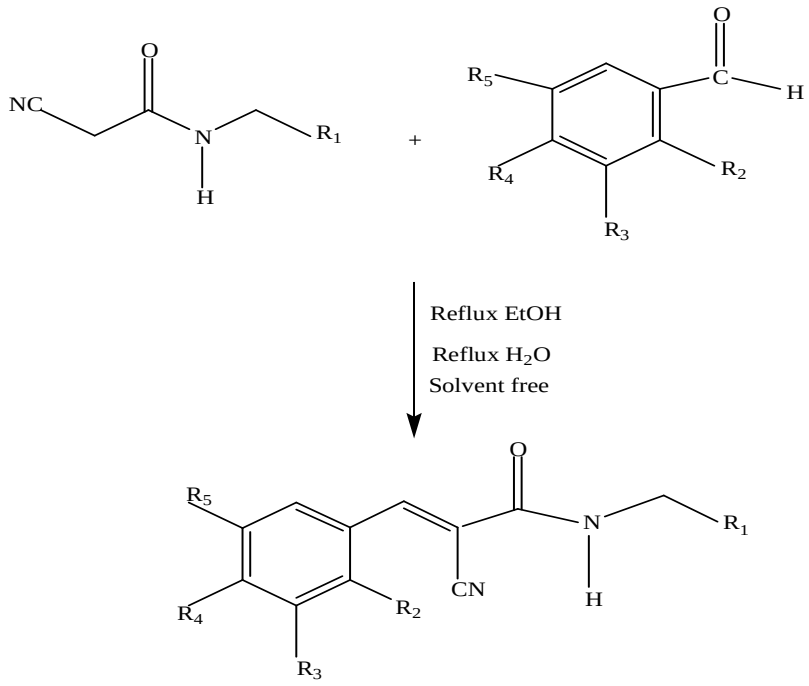


Figure 2.1. Knoevenagel condensation reaction [35]

Yoshizama et al [36] reported that the Claisen reaction of the ester substituted with a sterically bulky group proceeded very efficiently in solvent-free conditions (figure 2.2). In contrast, these reactions did not take place in solution procedures.

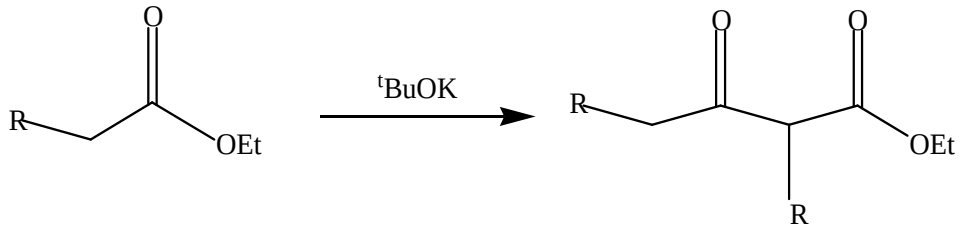


Figure 2.2. Claisen condensation reaction [36]

In the beginning, solvent-free reactions were done on a small scale usually in agate mortar and pestle, but nowadays industrial applications are starting to emerge.

For example Bose et al [37] have demonstrated that the Biginelli reaction, a reaction in which an aldehyde, a β-keto ester and urea or thiourea are involved to produce tetrahydropyrimidinones can be done using solvent-free conditions at industrial scale (figure 2.3).

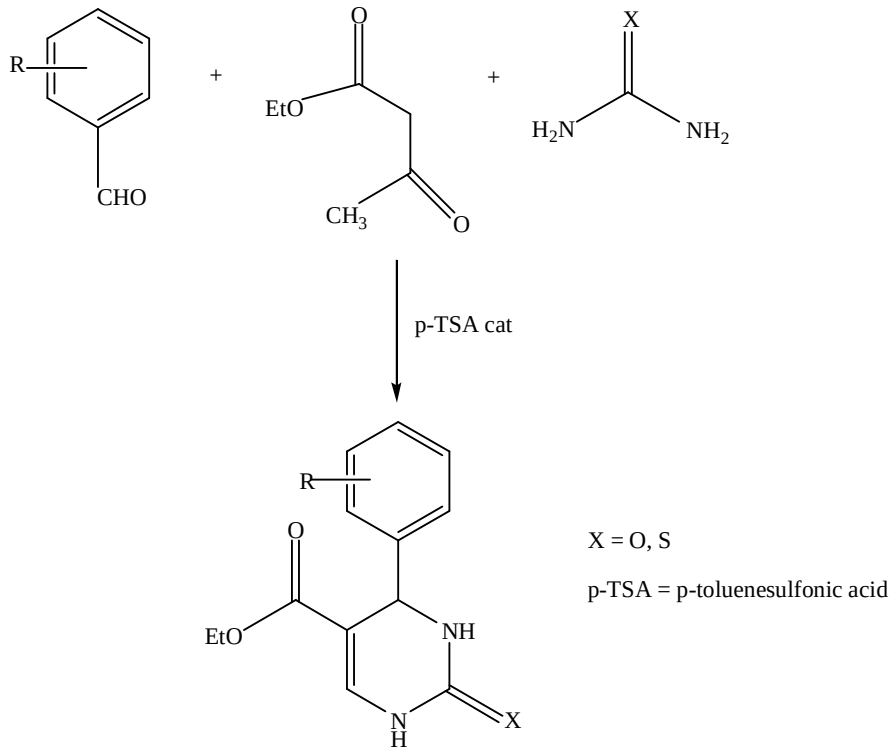


Figure 2.3. Biginelli reaction [37]

The yield is higher than that usually obtained from solvent procedures. Tanaka [34] presented a concise collection of organic chemistry reactions carried out in solvent-free procedures.

2.3.1.5. Solventless reactions in organometallic chemistry

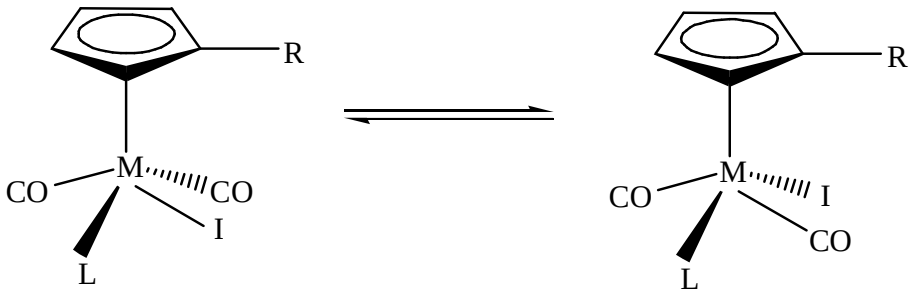
Most of the preparative work in organometallic chemistry was conducted in a homogeneous solution using an organic solvent [38]. The first case of solventless organometallic reaction appears to be that of Vaska in 1966 [39] on the reaction between $IrX(CO)(PPh_3)_2$ (X = Cl, Br, I) and HY (Y = Cl, Br, I) to give the oxidation addition reaction products $IRX(H)(Y)(CO)(PPh_3)_2$. Until recently, not much work followed this groundbreaking initiative.

However, solvent-free reactions of ferrocene derivatives have received attention in recent years. For example Liu and co-workers have reported that working in a dry medium, ferrocenylethene and 1, 5-diketone containing ferrocenyl derivatives can be synthesized in relatively easy reaction conditions [40, 41]. Solvent-free synthesis of ferrocenylimines from ferrocenylaldehydes and aromatic amines have also been reported to occur in excellent yields [42, 43].

Generally, solvent-free organometallic chemistry reactions reported in the literature can be grouped into three major categories: reactions between solid particles, surface organomtallic chemistry and solid-gas organometallic chemistry.

2.3.1.5.1 Solid-solid organometallic chemistry

The reaction takes place between two solid materials. Usually a ball mill mixing is required to ensure good contact between particles, a condition for the reaction to occur. Organometallic reactions taking place in solid state have been reported in the literature. For instance Nareetsile et al [44] reported the solid state isomerization of ttt-$RuCl_2(RNC)_2(PPh_3)_2$ to cct-$RuCl_2(RNC)_2(PPh_3)_2$ (R = 2,6–xylyl, ^{t}Bu, ^{i}Pr, benzyl, 2-OMe-4-Clphenyl). The solid state isomerization of substituted cyclopentadienyl molybdenum and tungsten derivatives have been also reported [45] (figure 2.4).



R = Me, ^{t}Bu

L = PPh_3, $P(O^{i}Pr)$

M = Mo, W

Figure 2.4. Isomerization reaction scheme for cyclopentadienyl Mo and W compounds [45]

Another example of solid state isomerization of cyclopentadienyl tungsten compounds has been recently reported by Bala and co-workers [46].

Migratory-insertion reactions have been found to occur in solventless conditions between $(\eta^5\text{-}C_5H_5)M(CO)_3Me$ (M = Mo, W) and phosphine or phosphite ligands [47, 48]. Generally, studies carried out in order to elucidate the mechanism of these solid-solid reactions revealed that they are diffusion controlled [49, 50, 51].

2.3.1.5.2 Surface organometallic chemistry

This category comprises the reactions dependent on the interactions between an organometallic precursor and mineral oxides such as silica, alumina, zeolites etc. to activate bonds in organometallic complexes. In the presence of a ligand, new organometallic compounds can be formed on the surface of those oxides using thermal or photolytic methods.

Compounds such as $[Ir(CO)_3Cl]_n$, $[Ru(CO)_3Cl_2]_2$ etc have been synthesized in high yields from the corresponding metal trichloride supported on a silica surface by reductive carbonylation at atmospheric pressure [52].
The reaction of $Ru_3(CO)_{12}$ with 2,2'-bypridine on SiO_2 has led after surface extraction with conc.HCl to the synthesis of $Ru(bipy)(CO_2)Cl_2$ [53]. More examples in which the organometallic reactions occur at the interface can be found in the literature [54].

2.3.1.5.3 Solid-gas organometallic reactions

It has been reported that the simplest reaction that can take place between a solid and a gas is a ligand displacement reaction [38]. Many reactions of this type have been reported and typically the incoming gaseous ligand is a small molecule such as CO, H_2 etc. For example the reaction of $Ir(COD)(PhCNL]^+$ (L = PPh_3, $AsPh_3$) with CO yielded an addition/displacement product $[Ir(COD)(CO)_2L]^+$ [55]. A displacement reaction between $Os_3(CO)_{11}L$ (L = MeCN, C_2H_4) and small molecules such as H_2, CO and NH_3 have been also reported [56].

2. 3. 2 Chemistry with green solvents.

If the use of a solvent in a particular reaction cannot be circumvented, the alternative way of doing benign chemistry is to use "green solvents" or safer solvents to replace the traditionally used Volatile Organic Compounds (VOCs) [57].

Some inconveniences related to the use of volatile organic solvents include the conjunctival irritation, nose and throat discomfort, headaches, allergic skin reactions, nausea, fatigue and so on [58]. To solve these problems, one would look for an alternative solvent which does not present the above mentioned constraints.

But before taking the option of using an alternative solvent as green, an assessment of the full life cycle assessment of the solvent should be done including the effect on the overall requirements for the application and the overall quantitative and qualitative assessment of waste generated from the application [33].

2. 3. 2. 1 Supercritical fluids: SCF

A triple point and a critical point are characteristics of all stable compounds [59]. The critical point is the end point of the liquid-gas line in the phase diagram. There the liquid and the gas become indistinguishable (figure 2.5).

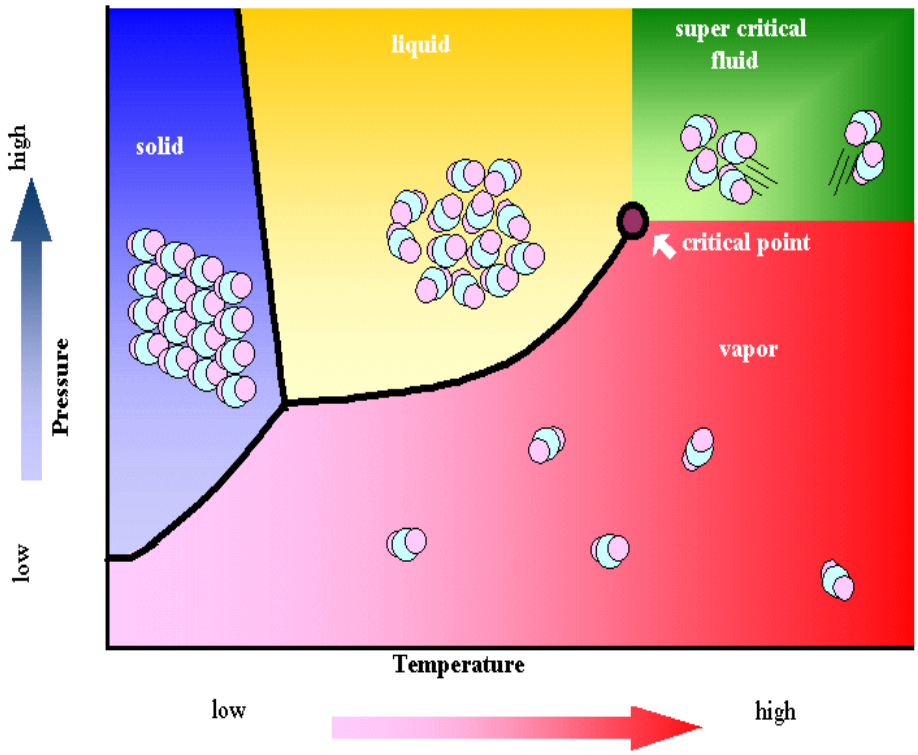


Figure 2.5. Phase diagram showing a supercritical state [60]

Different definitions have been proposed for a supercritical fluid state but the following seems to be the most precise: a supercritical fluid is any substance, the temperature and the pressure of which are higher than their critical values and which has a density close to or higher than its critical density [61].

In that region of the supercritical phase, the substance appears in a single condensed state and its properties are intermediate between those of a gas and those of a liquid [62]. Physical properties are significantly affected by changing either the pressure or the temperature. As the temperature of a liquid rises it becomes less dense and as the pressure of a gas rises it becomes denser; at the critical point the densities become equivalent. Generally, the density of a SCF is close to the density of the liquid and its viscosity is similar to that of a gas (see table 2.1).

Table 2.1. Typical liquid, supercritical fluid and gas properties [63]

	Liquid	**SCF**	**Gas**
Density (g/ml)	1	0.1-0.5	10^{-3}
Viscosity (Pa.S)	10^{-3}	10^{-4}-10^{-5}	10^{-5}
Diffusity (cm^2s^{-1}	10^{-5}	10^{-3}	10^{-3}

The critical points of some substances are reasonably accessible whilst it is not easy to reach critical points for others. For instance, Tc_{CO2} = 31°C; Pc_{CO2} = 73 atm, conditions which are relatively facile to realize but Tc_{H2O} = 374°C; Pc_{H2O} = 218 atm, conditions which are very difficult to achieve.

Difficulty to reach the critical point of a particular substance is one of the major handicaps which limit the use of supercritical fluids. Some typical data for common SCF's are given in table 2.2

Table 2.2. Critical data for some substances [61].

Substance	**T_c (K)**	**P_c (atm)**	**ρ (g/ml)**
Ammonia	405.4	113.2	0.24
Carbon dioxide	304.1	73.8	0.47
Ethane	305.2	48.7	0.20
Ethene	282.2	50.4	0.22
Fluoroform	298.9	48.2	0.62
Propane	369.7	42.5	0.22
Water	647.2	220.5	0.32
Ar	150.8	48.0	0.53
CH_4	190.6	45.8	0.16
Kr	209.4	54.3	0.93
Xe	289.8	58.0	1.15
C_2F_6	293	30.2	0.62
$CClF_3$	302.0	38.1	0.58
N_2O	309.7	71.7	0.45
SF_6	318.7	36.7	0.73
H_2S	373.5	88.9	0.35
Pentane	470.2	33.3	0.23
^{i}PrOH	508.5	47.0	0.27
MeOH	513.7	78.9	0.27
EtOH	516.6	63.0	0.28
^{i}BuOH	548.2	42.4	0.27
Benzene	562.1	48.3	0.30

However, from a green chemistry viewpoint, the use of SCFs presents many advantages although some disadvantages must be recognized. The discussion will be covered when assessing a specific SCF.

2. 3. 2. 1. 1 Supercritical Carbon dioxide: $ScCO_2$

$ScCO_2$ is the most commonly used supercritical fluid. Historically, $ScCO_2$ attracted the interest of researchers during the energy crisis in the 1970s [33]. At that time, distillation was the most costly operation in the chemical industry with regard to energy. Therefore, there was an obvious need for alternative solvents which do not have to be removed by distillation and $ScCO_2$ was among the good candidates. Advantages and disadvantages of using $ScCO_2$ are condensed in table 2.3 but in summary, because CO_2 is a non polar solvent, it has the ability of dissolving a wide range of non polar organic compounds having high volatility. In addition some compounds such as fluoropolymers which are only soluble in chlorofluorocarbons, dissolve in $ScCO_2$ [64]. This is a remarkable positive feature with regard to green chemistry issues, because in that sense, $ScCO_2$ can replace environmentally hazardous halogenated solvents. The ability for $ScCO_2$ to dissolve polar, ionic or polymeric compounds is exceedingly limited but alternative ways to overcome these problems have been proposed. For example in organometallic catalysis, the solubility of transition metal complexes can be achieved by modifying a ligand. By replacing an aryl group by an alkyl or alkoxy group, a complex can become easily soluble in $ScCO_2$ [33]. A suitable counter ion can dramatically improve the solubility of ionic metal complex in $ScCO_2$. For example $[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-$ and $CF_3SO_3^-$ are the typical counter anions used for extracting cationic Rh and Ir complexes.
CO_2 released from use as a solvent has the advantage over CO_2 produced from burning fossil fuels in the sense that it does not contribute to global warming. The reason could be that CO_2 produced during a chemical process is an industrial by-product (e.g. from ammonia manufacture) which would normally have been released to the atmosphere.

Due to its non polarity, one would expect $ScCO_2$ to dissolve hydrocarbons but this is not always the case and the reason for this is believed to be associated with its high quadrupole moment [65].

At the same time, this high quadrupole moment makes $ScCO_2$ a good solvent for small polar molecules like methanol and caffeine. Finally, the lack of polarity for $ScCO_2$ offers a positive impact for many reaction rates since CO_2 will not readily coordinate to many catalysts or solvate complexes.

Table2.3. Advantages and disadvantages of using $ScCO_2$ as a solvent [63].

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

Applications of $ScCO_2$

In homogeneous catalysis, the importance of SCFs was ignored until the early 1990s when Rathke [66] used $ScCO_2$ as a solvent in the hydroformylation of olefins. Since that time, many researchers have become interested in this unique reaction medium.

The uses of $ScCO_2$ can be grouped in two main categories [33]:

- $ScCO_2$ as extraction solvent

A widely established extraction process uses $ScCO_2$ for the decaffeination of coffee [66]. Before the 1980s, dichloromethane was the solvent used in this regard. Given the potential hazard of chlorinated compounds, it was wisely decided to replace dichloromethane by non harmful solvents like CO_2. The use of $ScCO_2$ as extraction solvent has also been extended to the food industry, for example, in the extraction of flavours from hops, extraction of essential oil etc. [67].

Finally, $ScCO_2$ is used in the dry cleaning process to replace the formerly used chlorinated solvents like carbon tetrachloride and perchloroethene [68]. $ScCO_2$ has been also used in the extraction of metals from aqueous solution [69].

- $ScCO_2$ as a process solvent

The most quoted application of $ScCO_2$ as a reaction solvent can be found in the polymerization area where $ScCO_2$ affords polymers of different molecular weights by altering the density of the medium through simple variation of pressure [66].

The big challenge in polymerizing polar materials (e.g. acrylates) in $ScCO_2$ is to build up the molecular weight to the stage where the polymer becomes commercially interesting before it falls out of solution.

Hydrogenation is also a very well established reaction in $ScCO_2$. The high miscibility of H_2 with $ScCO_2$ compared to its solubility in organic solvents is the main reason for choosing $ScCO_2$ instead of organic solvents in hydrogenation reactions [70].

2. 3. 2. 1. 2 Supercritical water: ScH_2O

Contrary to $ScCO_2$, conditions required to obtain ScH_2O are harsh (TcH_2O = 374°C; PcH_2O = 218 atm) [71]. This has limited the use of ScH_2O. From a solubility perspective, differences arise from what might be expected.

For instance ScH_2O dissolves hydrocarbons and gases such as oxygen, but does not dissolve ionic compounds like Na_2SO_4 [72]. In fact, the properties of ScH_2O are very different from those of ambient water. Under ambient conditions, liquid water is formed of a network of hydrogen bonds between molecules. At high temperatures (like Tc = 374^oC), this network is no longer there due to a very high thermal kinetic energy. Therefore, water at high temperature behaves like any other polar solvent [71]. This could then explain the unusual solubilities observed in ScH_2O. Gases are miscible to ScH_2O providing the opportunity to conduct chemistry in a single fluid phase which could only have been done in a multiphase system under conventional conditions [73]. The advantages of a single supercritical phase include high concentration of reactants and the lack of an interface to reduce the mass transport process.

Under supercritical conditions, H_2O is an excellent solvent for organic compounds. Due to the higher concentrations of H^+ and OH^-, ScH_2O is an effective medium for acid and base catalyzed organic reactions. In fact the concentration of H^+ is sufficient so that some acid catalyzed organic reactions would proceed without any added acid [74].

The use of ScH_2O can be limited for example by its high corrosivity especially when chloride-containing solutes are dissolved as well as the cost of specialized reactors in order to achieve the supercritical state.

Nevertheless, ScH_2O has many other interesting applications [75]:

- The synthesis of quartz crystals for mobile phones. They are formed from the reaction between silica and sodium hydroxide at around 400^oC and 700 bars. In this process, $NaFeSiO_4$ is used to protect the reactor from the high corrosivity of ScH_2O;
- Supercritical Water Oxidation, SWO, is a technique widely used in remediation and waste treatment. ScH_2O achieves this advantage by increasing the scope of products which can be mineralized and speeds up the process so that most organic materials can be completely oxidized within 2 minutes;
- Treatment of soils impregnated with industrial waste such as polychlorinated biphenols which are normally difficult to treat;

- Pyridine and nitrogeneous pollutants are successfully destroyed in SWO reactors at temperatures around 600°C.

2. 3. 2. 2 Ionic liquids

Based on the temperature, an ionic liquid can be defined as a salt with a melting temperature below the boiling point of water (100°C). The essential feature of ionic liquids is that they have a very wide liquidus range meaning that the interval of temperature between the melting point of an ionic liquid and its boiling temperature is significantly large [76, 77].

No molecular solvent can match the liquidus range of ionic liquids. Ionic liquids can be viewed as normal ionic materials such as NaCl, but ionic liquids are liquids at low temperature. Many terminologies are used to refer to ionic liquids [78]:

- Room temperature molten salts;
- Low-temperature molten salts;
- Ambient temperature molten salts;
- Liquid organic salts.

Historically, ionic liquids were firstly reported by Walden in 1914 when he reported on the synthesis of ethylammonium nitrate [79].

The ionic liquid was formed by the reaction between the concentrated nitric acid and ethylamine. After the reaction, water was removed by distillation affording a pure salt which was a liquid at room temperature.

By far, the most used and investigated ionic liquids are those based on 1,3-dialkylimidazolium cations [80, 81, 82].

These liquids possess many physical-chemical properties that qualify them as "tailor-made" green solvents for various reactions and processes: non volatile, liquids over a wide range of temperatures, low viscosity and higher density than most classical organic solvents, high thermal-electrochemical-chemical stability, dissolve a very broad spectrum of organic –inorganic compounds, typically non coordinating solvents, easily prepared from commercially available reagents through classical synthetic procedures etc. Some of the ionic liquids are now commercially available [83].

The "greenness" of ionic liquids is not as obvious as that of solvent-free systems or SCFs but some applications can be pointed out [84, 85]. These include:

- A very low vapor pressure, which, in combination with the fact that, ionic liquids can act as both catalyst and solvent is of a considerable interest. The very low pressure could make ionic liquids a viable alternative solvents for volatile organic solvents;
- Tunability: by changing the cation/anion ratio, properties such as acidity/basicity, melting point and viscosity can be affected;
- Stability at high temperatures (>300°C) which gives an opportunity to carry out reactions at high temperature and low pressure;
- Their immiscibility with organic solvents or water makes ionic liquids useful in product separation or in liquid-liquid extraction processes.

The main issues linked with the use of ionic liquids are centered on their eventual toxicity. Most ionic liquids have not been assessed and despite the potential for recycling, the fate and protocol for their ultimate disposal is not well known [86]. Another problem associated with the use of ionic liquids is their purification which is sometimes difficult [87, 76].

The assessment of the overall greenness of ionic liquids should also take into account their mode of synthesis for most of them are synthesized and purified using volatile and chlorinated solvents [86].

2. 3. 2. 3 Fluorous biphasic solvents

The fluorous biphase is a terminology used to characterize fully fluorinated hydrocarbon solvents (or other fluorinated inert materials like ethers) that are immiscible with organic solvents at ambient conditions [88, 89]. The word "fluorous" is used to express the philicity to the perfluoroalkanes with the analogy to "aqueous", a word which refers to the philicity to water [90]. The whole philosophy behind the use of fluorous biphasic solvents is that reactants and catalyst could be soluble in a fluorous phase under reaction conditions but products could readily separate into a distinct phase at ambient conditions (figure 2.6).

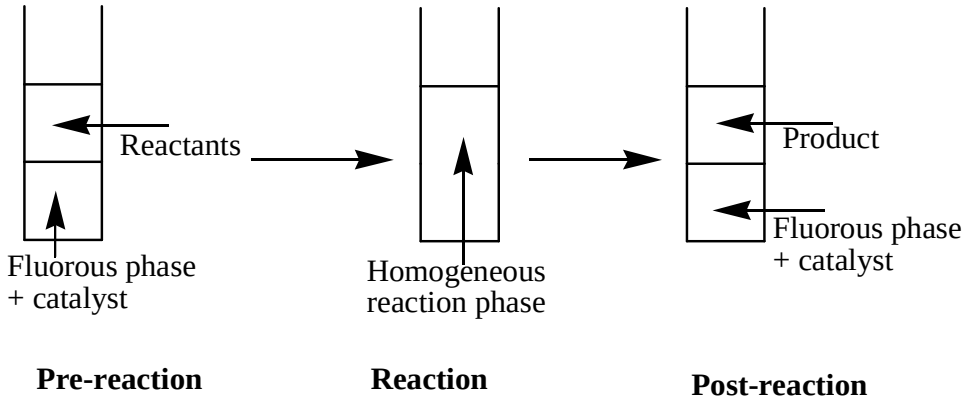


Figure 2.6. Fluorous biphasic solvents action

Two types of fluorous compounds can be distinguished [63]:

- Fluorous compounds with integral (permanent) fluorinated domains: e.g. $(C_6F_{14}CH_2CH_2)_3SnH$;

- Fluorous compounds with removable (temporary) fluorinated domains also called tags (figure 2.7).

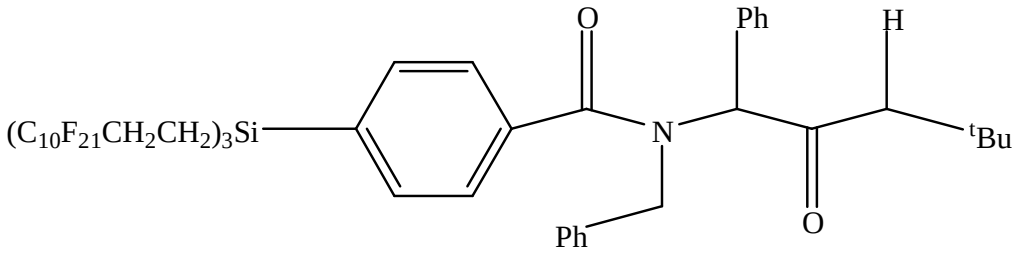


Figure 2.7. An example of a fluorous compound [63].

Tags or “pony tails” are often long perfluoroalkyl chains.
Apart from some low molecular weight solvents such as pentane and ether, perfluorocarbons are generally immiscible with water and organic solvents at room temperature [91]. Thus when mixed with water or organic solvents, the organic or water phase forms the upper layer, while the denser fluorous phase forms the lower layer. This gives an important role to the fluorous compounds in separation chemistry.

The behavior of fluorous/organic mixed systems was exploited successfully by Horváth and Rábai [92] in their landmark work in fluorous chemistry in 1994.
The use of fluorinated solvents can be classified into several categories among others:

- As a solvent in a reaction with fluorous reagents and/or fluorous substrates because of high solubility in fluorinated solvents;
- As an acidic catalyst or reagent for rearrangement, condensation or cleavage reactions;
- As amphiphilic solvents, easy to remove, with biphasic work-up;
- As alternative green reaction media for harmful or toxic chlorinated solvents.

The benign properties possessed by the perfluorinated compounds come from the stability of the C-F bond. These include their non toxicity, high level of inertness, high thermal stability, low-flammability and hydrophobicity [93].

Nevertheless, there are some issues regarding the use of perfluoro compounds.
These include the cost of the material, the "greenness" of their manufacture and to a lesser extent, their ultimate effect on the environment regarding their disposal. In fact, C_1 and C_2 fluorocarbons are potent greenhouse gases but compounds typically containing 6-10 carbons are much less volatile and they pose less of a threat.
The use of a non - polar fluorous phase works better and the separation of the product is facilitated when reactants are non polar and the polarity of the product is relatively high.

2. 3. 3 Chemistry using Microwaves

Microwave radiation has a wavelength regime between 1mm and 1 m in the electromagnetic spectrum (frequencies of 30GHz to 300MHz). It lies between infrared radiation and radio frequencies. The interaction of matter with microwave radiation results in a temperature enhancement [94]. A simplified mechanism to explain the interaction can be summarized as follow [95]: when a substance possessing a dipole moment like H_2O is subject to electromagnetic radiation, it will attempt to align to the electromagnetic field by rotation.
In liquid substances this rotation causes friction between neighbouring molecules resulting in a temperature rise. The heating rate is influenced by the rate of rotation and the radiation frequency. The rise of temperature from the interaction of a substance with radiation is exploited by chemists to initiate chemical transformations.

Table 2.4: Effect of microwave heating on some solvents [95]

Solvent	**T(^{o}C)**	**Boiling point (^{o}C)**
Water	81	100
Methanol	65	65
Butanol	109	117
1-Hexanol	92	158
Chloroform	49	61
Acetone	56	56
Hexane	25	68
Heptane	26	98
Carbon tetrachloride	28	77

However, all radiation cannot lead to a temperature rise: at high frequencies, the change in the direction of the field is too quick to allow rotation to occur, and no heating effect would occur; at low frequencies, the rate of rotation is too slow resulting in a minimal heating effect; in the microwave region of the spectrum, the rates of rotations are good enough to produce a rise of temperature in dipolar substances. The effect of microwave radiation on some solvents is presented in table 2.4.

This said, non polar substances cannot be heated by microwave radiations. One of the ways of solving this problem is to add a small amount of a polar substance to the non - polar material. The mixture will quickly achieve a uniform temperature under irradiation. Gases are not also heated by microwave radiation due to the long distances between molecules.

If the solution contains ions, the heating is achieved by conduction. The electric field will move the ions through the solution and the kinetic energy resulting from collisions will be converted into heat [96].
One of the advantages of using microwaves as a source of heat is that the heat is directly imparted to the reaction medium rather than to the walls of a reaction vessel as is the case for conventional steam or oil baths. As a result, chemical reactions can be performed in an extremely short time compared to the traditional methods of heating.

Solvent free microwave assisted reactions [97, 98].

These types of reactions are suitable for microwave heating since the radiation is directly absorbed by the reactants giving enhanced energy efficiency. No energy conduction is required. Moreover, some non crystalline solid supports such as some metal oxides are poor at conducting heat but absorb microwave energy. For instance, simply by mixing a solid oxidizing agent with a range of secondary alcohols and irradiating for a period less than 1 min, ketone yields higher than 90% are obtained (figure 2.8).

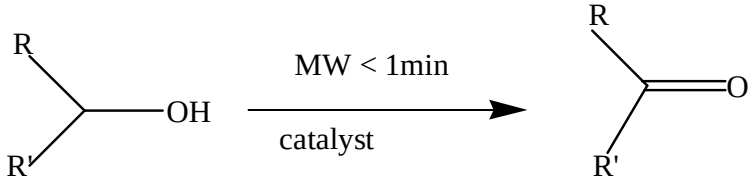


Figure 2.8. Reaction of secondary alcohols under microwave irradiation

The "greenness" of solvent-free microwave reactions resides in the elimination of the use of volatile and toxic organic solvents, thus enabling the neat reactants to undergo facile transformations at atmospheric pressure. This facilitates easy isolation of the products and promotes safety associated with handling the reaction in open vessels, thus culminating in chemical processes with unique attributes such as faster reaction kinetics, higher product yields and safer manipulations [99].

The main issue associated with the use of microwaves is that non polar substances cannot be heated.

2. 3. 4 Sonochemistry

The term sonochemistry refers to chemical reactions induced by ultrasound [100]. Ultrasound is a sound wave with a frequency higher than those detectable by the human ear i.e. around 18 KHz.

Like microwaves, the interaction between matter and ultrasound results in a temperature rise but the mechanism is different [101].

When a sound wave passes through a liquid medium, it causes the molecules to oscillate around their mean position. During the compression phase, the average distance between molecules is reduced while it is increased during rarefaction phase. In the rarefaction cycle, attractive forces of the molecules may be overcome and bubbles could be formed. This phenomenon is called “cavitation” [102]. If internal forces are great enough to cause collapse of these bubbles, very high local temperatures (~5000°C) and pressures (>1000 bars) may be created. It is these temperatures and pressures which initiate chemical transformations.

The sound waves are generated by converting electrical energy using a transducer. The main advantage of the use of ultrasound in chemistry is that the technique does not require any special characteristic of the system in order to function [103]. For instance, microwave chemistry occurs with dipolar species while sonochemistry requires only the presence of a liquid to transmit energy.

2. 3. 5 Catalysis and green chemistry.

One of the key technologies to achieve the objectives of green chemistry is the use of a catalyst in a chemical transformations [104]. Traditionally, a catalyzed reaction presents many advantages over uncatalyzed reaction. Apart from the fact that some reactions under specified conditions do not proceed at all in the absence of a suitable catalyst, many others are dramatically accelerated by the use of a catalyst [105].
The action of a catalyst consists in lowering the activation energy of the reaction resulting in quicker kinetics due to a lowered energy barrier. The design and the application of new catalysts and catalytic systems achieve simultaneously the double goal of environmental protection and economic benefit. The numerous green chemistry benefits offered by the use of catalysts include: lower energy requirement, catalytic versus stoichiometric amounts of materials, increased selectivity and decreased use of processing and separation agents, use of less toxic materials [106]. Separation through distillation or extraction may no longer be needed when working under heterogeneous catalysis conditions. Nevertheless, new catalysts and catalytic technologies need to be developed to replace some hazardous catalysts still in use [107]. Many studies have been performed in the field of catalysis that have shown the advantages from a green chemistry viewpoint. Some examples are listed below:

1. Cheng et al [108] have developed a catalyst which affords polycarbonate products at enhanced rates using milder conditions than previous catalysts.

2. Conventionally, the synthesis of methyl anisoles, industrial products important in the manufacture of agrochemicals, proceeds via a combination of cresols with a methylating agent such as dimethyl sulfate and alkali in THF. The process itself is atom inefficient generating a salt waste and the reagents are corrosive and toxic.

A recently developed catalyst consisting of a cesium loaded silica (Cs/SiO_2) achieves vapor phase methylation of cresols with high selectivity and conversions [109].

3. The cleavage and removal of thioacetals and thioketals conventionally use heavy metals such as mercury (II) chloride and selenium dioxide. Bandgar and co-workers [110] have developed a catalytic mode to remove those carbonyl protecting groups: using microwave radiation and solvent free conditions and a catalytic amount of kaolinitic clay, the thioacetals and thioketals liberate the carbonyl compounds in good yields. These examples show the importance of the use of the catalyst from the perspective of achieving the goals of green chemistry.

2.4. Barriers to green chemistry development

Green chemistry is an approach dealing with pollution prevention problem. Although this approach has so far yielded to dramatic improvements to the general state of the environment (air, water, soil), there are still some handicaps blocking its spreading all over the world. These can be broadly categorized into three groups: knowledge, legislation and economic barriers [111, 112, 113].

2.4.1. Knowledge barrier

There is a philosophy believed to have introduced by Parcelus many years ago that ‘everything is poison depending on the dose’ [14]. This rationale is sometimes used to justify the inertia of some people as for them, if everything is toxic nothing can be done to control the toxicity. It is true that the excess of anything leads most of times to a negative consequence but all substances are not equally hazardous. The level of toxicity varies from a compound to another.

Therefore, it is always important to minimize the risk of exposure to the hazardous substance, avoid their production and use wherever possible and look for alternative non hazardous substances in order to protect the human health and the environment in general [114].

Another problem related to the knowledge issue is that the toxicological data are only available for a very low percentage of the total number of known chemical compounds [115]. This may serve as a pretext to the inaction of some people. However, correlations within chemical classes have been extensively established. Hence, if no toxicological data are available for a particular chemical substance, it is reasonable to assume that it will behave similarly to other compounds belonging to the same class for which toxicological data are known.

In order to overcome this knowledge barrier, it has been proposed that school and university chemistry courses should contain green chemistry topics so that when graduates enter the industry, they are already conscious about the waste generation, safer synthetic design and all other green technologies [116, 117].

2.4.2. Legislation barrier

In general, there is a lack of legislation against environmentally unfriendly processes. As a consequence, the less environmentally friendly procedures are still carried out and no legal action can be taken because there is no law related to the matter. This plays a significant role in the discouraging the green chemistry development [118].

2.4.3. Economic barrier

Green technologies are sometimes considered as being more expensive than the classical technologies.

When this perception is coupled with the lack of knowledge about the new technology to be introduced (no demonstration facilities, no case study for example), this results in hindering the adoption by the industry of the results coming from the research [119].

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