# Fluorescence Studies in Room Temperature Ionic Liquids

**Anunay Samanta** *

This short article provides a brief introduction on these novel and promising substances and it highlights some of the physicochemical properties of these substances that one can obtain by measuring the fluorescence response of some suitable probe molecules in these media. Literature is provided for the readers interested in additional information on these substances including their utility in various fundamental studies and applications.

Room Temperature Ionic Liquids (RTILs) have attracted a lot of interest during the past decade as fascinating novel substances having potential to become a 'green' alternative to the highly volatile organic compounds (VOC) that are used as conventional solvents. Room temperature ionic liquids (RTILs) are salts and like any other salt, they consist entirely of ions. However, unlike the common salts, which are ionic solid at room temperature, these salts (Chart 1) have low melting point and are liquid at ambient conditions. The low melting points of the RTILs are primarily attributed to (i) relatively weak electrostatic forces between the constituent ions due to their bulky nature and charge delocalization, and (ii) poor packing of the ions due to unsymmetrical substitutions. In essence, RTILs are salts, which cannot form well-packed solids. As it is possible to design and develop a huge number of these salts

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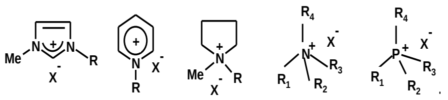
with tailor-made properties by appropriate selection of the anionic and cationic constituents, these are called ‘designer solvents’.



X= $AlCl_4$, $BF_4$, $PF_6$, $SbF_6$, $(CF_3SO_2)_2N$, $EtSO_4$; R = alkyl group

***Some commonly used RTILs***

Because of their negligible vapor pressure, ability to dissolve both inorganic and organic compounds, high thermal stability and conductivity, the RTILs have gained immense popularity as potential ‘green’ alternative to the volatile organic solvents used in various synthetic, electrochemical and separation processes. However, in recent years more attention is being paid to explore the utility of these substances in specific applications such as in the synthesis of nanomaterials, as mobile phase in HPLC, for enzyme stabilization, as biocatalysts, as gas sensor, as supporting electrolyte for solar and fuel cells, etc. Optical absorption and fluorescence studies in these media have provided a rich understanding of some of the physical properties of these substances such as polarity, viscosity, microheterogeneity.

Utilisation of these substances as media for spectral studies requires that these are transparent, colourless and nonfluorescent liquids. However, unless one takes utmost care during the synthesis, very often the RTILs are found to be yellow in color. Studies on the optical properties of the RTILs have revealed that the imidazolium ionic liquids absorb in the near

UV region due to the imidazolium moiety. Moreover, these liquids exhibit weak emission with the fluorescence quantum yield dependent on the excitation wavelength. Therefore, the optical properties of the RTILs do pose some limitations to the photophysical studies in these media; in particular, those involving substances that absorb in the UV region and which are not strongly emitting. However, the studies carried out so far clearly indicate that these limitations are not so serious and the opportunities provided by these novel solvents are really huge and left largely unexplored.

Polarity is one of the key properties of a medium. The polarity of several imidazolium ionic liquids has been estimated by measuring the wavelength corresponding to emission maxima of solvent sensitive fluorescent probes such as coumarin 153 (C-153), 4-aminophthalimide (4-AP) and 4-dimethylaminophthalimide (4-DAP) (Chart 2). These measurements have indicated that the RTILs are more polar than acetonitrile but less polar than methanol. A narrow range of the polarity of a large number of RTILs is the result of the leveling effect of C(2) hydrogen atom of the imidazolium cation as the solute-solvent hydrogen bonding interaction energy is overwhelmingly larger than that due to the other weaker interactions.

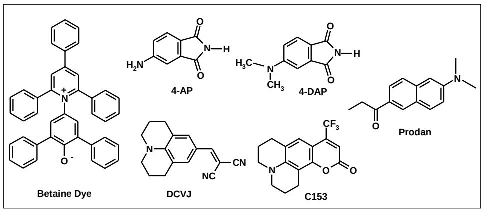


**Chart 2.** *Structures of some common probe molecules used for the determination of polarity, viscosity and solvation response of RTILs.*

Fluorescence measurements have also been used for the measurement of microviscosity of a variety of microheterogeneous systems like ionic liquids. One can use steady-state fluorescence anisotropy measurements to determine the microviscosity using the Perrin's relation

$$\frac{r_0}{r} = 1 + \frac{kT\tau}{\eta_m V_0}$$

where, r and $r_0$ are the measured and limiting fluorescence anisotropies, respectively, $\tau$ is the excited state lifetime and $V_0$ is the hydrodynamic volume of the probe. One can also use molecular probes like pyrene which forms excimer in the excited state for the measurement of microviscosity. In this case, the microviscosity is estimated from the ratio of the fluorescence intensities of the monomer to the excimer. The microviscosity of several RTILs has been estimated employing molecular systems, termed as 'molecular rotors', whose fluorescence quantum yield is highly sensitive to the viscosity of the medium. These measurements reveal that the microviscosity of the RTILs can be quite different from their bulk viscosity.

Photo-excitation of a polar molecule usually results in an enhancement of the charge separation leading to an increase in the dipole moment of the molecule. The reorientation of the solvent dipoles around an instantly created solute dipole on photo-excitation is termed as solvent relaxation. The solvent relaxation provides insight into the nature of the solute-solvent and solvent-solvent interactions. Solvation time can be estimated from the time-dependent fluorescence Stokes shift of dipolar molecules such as coumarin 153 (C-153), 4-aminophthalimide (4-AP), and 6-propionyl-2-dimethylaminonaphthalene (PRODAN), shown in Chart 2. That solvation dynamics in RTILs is slow is evident from the fact that all these dipolar molecules exhibit a wavelength dependent fluorescence behavior shown in the following figure.

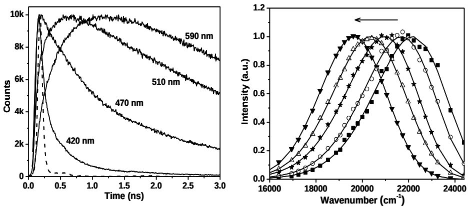


**Figure 1.** *Typical wavelength-dependent emission decay profiles and time-dependent fluorescence Stokes shift of a dipolar probe molecule*

Following the pioneering work of Karmakar and Samanta, many researchers have studied the solvation dynamics in RTILs, which is mechanistically different from that in molecular solvents. These studies have revealed that solvation in RTILs is a slow process and is dependent on the viscosity of the medium. However, a part of the dynamics is ultrafast in nature. The mechanism of solvation dynamics and the time scale of the ultrafast dynamics are still far from clear.

Even though the RTILs appear quite homogeneous by naked eye, several experimental and simulation studies have revealed that these are microheterogeneous systems comprising of hydrophobic and hydrophilic domains like micelles, reverse micelles, lipid bilayers, vesicles, proteins, membranes etc. The microheterogeneity of the RTILs is perhaps reflected in the excitation wavelength dependent emission behavior or red-edge effect of some molecular systems. While some experimental and simulation studies have indicated indirect evidence of the microheterogeneity, small and wide angle X-ray (SWAX) studies have shown that these heterogeneities are of the order of a few nanometers and the size is proportional to the alkyl chain length.

Several photo-induced electron transfer (PIET) reactions have recently been studied in RTILs by monitoring the fluorescence behavior of the systems. These studies have shown that even though PIET reactions are quite efficient in these media, the yield of the products is very poor owing to rapid back electron transfer reaction.

This short note highlights only some specific areas of research involving the RTILs thus leaving many important areas completely untouched. In order to find out some of the possibilities that a huge number of these designer liquids can offer to us it is recommended that the interested reader browse through some of the references, in particular, the review articles.

***Suggested Reading:***

1. MacFarlane, D.R.; Forsyth, M.; Howlett, P.C.; Pringle, J. M.; Sun, J.; Annat, G.; Neil, W.; Izgorodina, E. I. *Acc. Chem. Res*. **2007**, *40*, 1165.
2. Plechkova, N. V.; Seddon , K. R. *Chem. Soc. Rev.* **2008**, *37*, 123.
3. Samanta, *A. J. Phys. Chem. Lett*. **2010**, *1*, 1557.
4. Abedin, S. Z. E.; Endres, F. *Acc. Chem Res.* **2007**, *40*, 1106.
5. Borra, E. F.; Seddiki l, O.; Angel, R.; Eisenstein, D.; Hickson, P.; Seddon, K. R.; Worden S. P. *Nature* **2007**, *447*, 979.
6. Earle, M. J.; Gordon, C. M.; Plechkova, N. V.; Seddon, K. R.; Welton, T. *Anal. Chem.* **2007**, *79*, 758.
7. Reichardt, C. *Green. Chem*. **2005**, *7*, 339. .
8. Santhosh, K.; Banerjee, S.; Rangaraj, N.; Samanta, A. *J. Phys. Chem. B* **2010**, *114*, 1967.
9. Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, *106*, 4447, 6670.
10. Jin, H.; Baker, G. A.; Arzhantsev, S.; Dong, J.; Maroncelli, M. *J. Phys. Chem. B* **2007**, *111*, 7291.
11. Mandal, P. K.; Sarkar, M.; Samanta, A. *J. Phys. Chem. A* **2004**, *108*, 9048.
12. Lopes, J. N. C.; Padua, A. A. H. *J. Phys. Chem. B* **2006**, *110*, 3330.
13. Wang, Y.; Voth, G. A. *J .Am. Chem. Soc*. **2005**, *127*, 12192.
14. Triolo, A.; Russina, O.; Bleif, H. J.; Cola, E. D., *J. Phys. Chem. B*, **2007**, *111*, 4641.

# Green Chemistry: Brief Introduction

**Sourav Basu ***

## Chemistry: A Brief History

Fire is the first man made chemical reaction known to civilization where an organic compound reacts with oxygen to produce energy in the form of heat and light and in most cases carbon dioxide, other oxides (based on the source of the ignited mass) as by products of the reaction. However, if we look back towards the origin of life all biochemical reactions happening in the living organism since that period. First industrial application of chemical reaction is metallurgy in 2500 BC and then came atomism, alchemistry and finally the era of modern chemistry in 1700 BC. This resulted to almost a revolution in human live for past 300 years. In modern life chemistry is an integral part of everything around. It's a long list and few representative examples are (i) Energy: Cracking of Crude - Catalysis (ii) Pharmaceutical: All Medicinal Products (iii) Crop Protection: Insecticides/Pesticides/Herbicides (iv) Animal Care: Live Stock, Poultry, companion animal (v) Materials: Polymer, Paints, Medical Devices (vi) Cosmetics: Fragrances, hair care (vii) Food and Food Additives: Health Food Supplements etc.

## Chemistry and Environment

Despite chemistry being an integral part of human civilization

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today it's to some extent an unnatural science of making and breaking bonds. Every chemical process involves energy in form of heat, reagents and catalysts and always end up creating a number of bi-products which are not environment friendly and even lethally toxic in several instances. Such bi products if not controlled and treated properly are termed as pollutant and potentially can create major harm to the living world including human beings, animals and plant kingdom. Several such disasters involving chemical pollutants took place in the history of human civilization in several countries including India.

## Green Chemistry

Chemists and industrial chemical engineers working across the world from early 1990s focused their attention in developing chemical processes which can minimize such issues mentioned above. An organizational movement towards that goal resulted in creating benchmarks and goals for an improved subject which we popularly mention as "Green Chemistry" today. Green chemistry is guided by some principles which are called as "Rule of 12". This include following things.

(i) Prevention of waste – Minimal waste generated in a process apart from the product of interest
(ii) Atom economy – Number of atoms in reactants and products have minimal
Difference in number

(iii) Generation of Eco friendly bi-products
(iv) No toxicity to human health and the environment.

(v) High efficacy low toxicity products – Products which are required in low amount for their function especially medicines, agrochemicals etc.
(vi) The use of solvents, separation agents, etc. should be made unnecessary Energy minimization
(vii) A raw material or feedstock should be renewable
(viii) Reduce derivatives - Unnecessary derivatization
(ix) Catalytic reagents are superior to stoichiometric reagents.
(x) Chemical products must at the end of their function they degrade
(xi) Analytical needs to be developed for real-time, in-process monitoring
(xii) Clean process with minimal hazard

Final goal of the process is to mimic biochemical reactions which happen in nature. If will look at photosynthesis this is an example of an ideal green reaction as the reaction is catalytic, employs natural energy i.e. sunlight produces Oxygen as byproduct, provides highest atom economy, creates a product with 0 Toxicity, end product is degradable in the course of time.

There are several quantitative measures available with modern chemists to rank his process in the scale of green attributes. Some of these things are (i) Effective Mass Yield (ii) Carbon Efficiency (%) (iii) Atom Economy (iv) Reaction Mass Efficiency (v) E-Factor etc.

In our recent activities towards green chemistry we have developed an efficient protocol for the synthesis of benzoquinoline core via Michael addition of indole and pyrrole to novel cyclic nitrotetraline analogues. These classes of compounds are extremely important in pharmaceutical as a basic scaffold for drug molecules in different disease areas. The procedure was simple, and worked successfully without using any catalyst or organic solvent. A typical procedure involves mixing two compounds in water and heating the mixture at 100oC. A number of benzoquinoline analogues have been synthesized using this procedure in excellent yield. Transformation of these compounds towards a number of therapeutic targets is currently underway.

***References:***

1. United States Environmental Protection Agency (www.epa.gov) and references cited therein
2. Unpublished results, TCG Lifesciences: Water as a solvent in important organic transformations.
3. http://en.wikipedia.org/wiki/History_of_chemistry

# Organic Reactions in the Perspective of Green Chemistry

**Sanjay Bhar ***

The introduction of large amount of any chemical substance in the environment, even to eradicate disease, has the potential for long-term and far-reaching effects that may be very difficult to predict. Therefore, adequate caution must be taken about our fragile environment. Our well-intentioned intervention too often upsets the critical balance of nature and, as a result, we inadvertently do more harm than good. Therefore, development, now-a-days, is associated with the term sustainability which means "to meet one's need in the present generation without any compromise with the ability of the future generation to meet their own need". After various disasters caused due to over-exposure and leakage of different chemical compounds, the scientific community all over the world began to pursue practical elegance to develop alternative protocols for important chemical transformations which are intellectually logical as well as technically efficient. Thus a new attitude in chemical endeavour has emerged which is known as Green Chemistry.[1] Practice of Green Chemistry has become a focal theme of chemical pursuit in recent times to ensure chemical safety in this vulnerable world as it is essential to establish sustainability.[2]

United States Environmental Protection Agency has attested "Twelve Principles of Green Chemistry" (originally proposed by Paul

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Anastas and John Warner) which include a) prevention of waste, b) design of safer chemicals and products, c) design less hazardous chemical synthesis, d) use of renewable feedstocks, e) use of reagents in catalytic amounts rather than stoichiometric, f) minimization of derivatization, g) maximization of atom economy, h) use of safer chemicals and solvents, i) increase of energy efficiency, j) design of chemicals and products to degrade after use, k) in-process monitoring to prevent pollution and l) minimization of potential for accidents. In this light Pfizer company has classified the solvents in three categories from the standpoints of toxicity and risk factors. Solvents like diethyl ether, chloroform, 1, 2-dichloroethane, carbon tetrachloride, benzene, pentane, hexane, pyridine etc. are totally undesirable. Solvents like toluene, acetic acid, DMSO, ethylene glycol, acetonitrile are usable with some reservations. Most preferred solvents include ethanol, methanol, n-propanol, isopropanol, n-butanol, t-butanol, acetone, ethyl methyl ketone, ethyl acetate, isopropyl acetate etc. Quite obviously, water is present at the top of this list. The desirable alternatives have also been proposed. Dichloromethane is the most preferred one among all halogenated solvents and if possible, to be replaced with ethyl acetate. Benzene is to be substituted with toluene. It is preferred to use t-butyl methyl ether instead of diethyl ether for solvent extraction. Heptane is the preferred alternative of pentane and hexane.

The chemists all over the globe are trying to develop novel alternative methods where the use of toxic organic solvents as the reaction medium can be avoided. At times, novel results have been obtained under alternative conditions which are neither observed nor anticipated in conventional methods.[3]

Water is the most benign reaction medium from the environmental perspective. Several organic reactions in aqueous condition have been developed. According to R. Breslow, [4+2]- cycloaddition reaction occurs at much higher rate with greater *endo*-selectivity in water compared to the analogous reactions in various organic solvents. In course of our pursuit[4] to utilize water as the most benign medium for organic reactions, a novel aluminium-mediated protocol for highly chemoselective pinacol coupling of aromatic aldehydes in aqueous medium was developed[4a] where the role of water towards the efficacy and diastereoselectivity of the said process has been demonstrated. Water also played remarkable role[4b] to dictate the reaction outcome in the aluminium-mediated reduction of diaryl ketones. Aryl alkyl ketones and cycloalkanones were obtained chemoselectively from their oximes and semicarbazones in aqueous phosphoric acid without any organic co-solvent in the reaction medium.[4c] On-water reactions, a recent development involving substrates sparingly soluble or insoluble in water, have gained extensive importance and popularity. An efficient "On-water" protocol[4d] for the synthesis of β-bromostyrene through the bromodecarboxylation of substituted cinnamic acids came out using eco-friendly reagents like hydrogen peroxide as the oxidant and potassium bromide as the source of bromine.

Surface-mediated reactions under solvent-free condition constitute another chapter in connection to eco-compatibility. Inorganic supports like alumina, silica gel, zeolite etc. have been successfully utilized as supports for various organic transformations under solvent-free condition with improved yield and better selectivity. The solid supports often possess microenvironments with acidic and basic sites to polarize the substrates and reagents held at close proximity. So the entropy of activation is decreased and the reaction is accelerated.

Exploring the attributes of supported reagents, various 4, 4-*bis*-functionalized-1, 6-dienes and 1, 6-diynes were synthesized[4e] in dry media on the surface of neutral alumina impregnated with sodium or potassium alkoxide. Excellent regioselectivity was observed and various usual side reactions were minimized. The reactions in dry state adsorption condition were found to be faster and superior to those in solutions. These results show that the normal reactivity of certain reagents can be attenuated for our benefit if it is adsorbed on some chemically robust support. The products are obtained with better purity due to immobilization of the by-products on the support. This was aptly demonstrated using PCC adsorbed on neutral alumina, where chromium by-products were immobilized on alumina support. It was found[4f] that several constitutionally varied aliphatic primary alkanols gave the corresponding alkyl alkanoates under solvent-free conditions without a detectable trace of the aldehydes, whereas, benzylic primary alcohols (unsubstituted, substituted and vinylogous), under the same oxidative condition produced the corresponding aldehydes without further oxidation to the corresponding carboxylic acids or ester. This result was totally unprecedented and demonstrated the very efficacy of the solvent-free protocols compared to the reactions in conventional organic solvents. The efficacy of solvent-free reactions using supported reagents to achieve chemoselectivity and reuse of renewable resources was observed during protection of carbonyl groups on alumina-sulfuric acid support.[4g]

The novelty of solid phase and solid state organic reactions has been well-documented with numerous examples. Many such reactions occur more efficiently on microwave exposure. Microwave oven is called as the "Bunsen Burner of 21st century" because of the additional effects of microwave irradiation compared to mere thermal activation. So, it is very important to distinguish between "thermal" and "non-thermal" microwave effects to establish the "specific microwave effect" in microwave-assisted reactions. This was demonstrated in course of the study of microwave-assisted ammonium formate-mediated solvent-free Knoevenagel reaction[4h] and Hantzsch synthesis of dihydropyridine.[4i]

The importance of design and development of alternative protocols for organic transformations does not merely concern with the improvement of environmental performance but also lies in the growth and nourishment of the knowledge bank of chemical science with novel findings. Green Chemistry is not a solution to all environmental problems but the most fundamental approach to prevent pollution.

The very concept of Green Chemistry needs to be percolated and its practice should be culminated among the students from the higher secondary and undergraduate levels through re-design and requisite modification of their practical curricula with the incorporation of different experiments having some green contexts in terms of safety and use of environmentally benign reagents, solvents and methods. Preparation of benzilic acid in solid state and carrying out benzoin condensation using thiamine hydrochloride as an eco-friendly alternative of potassium cyanide are two good choices for this purpose. The long-cherished practice of detection of special elements in organic compounds using metallic sodium should be abandoned during qualitative analysis to avoid the risk of explosion and fire hazard. Zinc-sodium carbonate mixture can be used as its safe alternative. To practice Green Chemistry as much as practicable becomes very urgent in the present ecological perspective which can altogether improve and modulate our attitude in all spheres of life for the overall benefit of human civilization from the standpoint of sustainability.

***References:***

1. (a) Anastas P. T.; Warner, J. C. *Green Chemistry- Theory and Practice*, Oxford University Press, Oxford, **1998**. (b) Anastas P. T.; Williamson, T. C. *Green Chemistry-Frontiers in Benign Chemical Syntheses and Processes*, Oxford University Press, Oxford, **1998**. (c) Rajappa, S. *Emerging Eco-friendly Alternatives for the Fine Chemical Industries*, Sevak Publications, Mumbai, **2000**. (d) Dicks, A. P. *Green Chemistry Letters and Reviews*, **2009**, *2*, 9-21.

2. Djerassi, C. *Angew. Chem. Int. Ed. Engl*. **2004,** *43*, 2330-2332.

3. (a) Metzger, J. O. *Angew. Chem. Int. Ed. Engl*., **1998**, *37*, 2975-2978. (b) Tanaka, K.; Toda, F. *Chem. Rev*. **2000**, *100*, 1025-1074. (c) Cave, G. W. V.; Raston, C. L.; Scott, J. L. *Chem. Commun*. **2001**, 2159-2169. (d) Braga, D.; Grepioni, F. *Angew. Chem. Int. Ed. Engl*., **2004**, *43*, 4002-4011. (e) Antesberger, J.; Cave, G. W. V.; Ferrarelli, M. C.; Heaven, M. W.; Raston, C. L.; Atwood, J. L. *Chem. Commun*. **2005**, 892-894.

4. (a) Bhar, S.; Panja , C. *Green Chemistry* **1999** , *1* , 253-255. (b) Bhar, S.; Guha, S. *Tetrahedron Lett.* **2004**, *45*, 3775-3777. (c) Bhar, S.; Guha, S. *Synth. Commun*. **2005**, *35*, 1183-1188. (d) Roy, S.; Bhar, S. *Green Chemistry Letters and Reviews* **2010**, *3*, 341 – 347. (e) Bhar, S.; Chaudhuri, S. K.; Sahu, S. G.; Panja, C. *Tetrahedron* **2001,** *57***,** 9011-9016**.** (f) Bhar, S.; Chaudhuri, S. K. *Tetrahedron* **2003**, *59*, 3493-3498. (g) Saha, M.; Bhar, S. *Green Chemistry Letters and Reviews* **2011**, *4*, 137 – 142. (h) Saha, M.; Roy, S.; Chaudhuri, S. K.; Bhar, S. *Green Chemistry Letters and Reviews* **2008**, *1*, 113-121. (i) Saha, M.; Roy, S.; Chaudhuri, S. K.; Bhar, S. *Green Chemistry Letters and Reviews* **2008**, *1*, 99-102.

# Contribution of Solid Supported Metal Nanoparticle in Green Chemical Process Development

**Pralay Das ***

## Introduction

Development of a safe, simple and environmentally benign chemical process to produce a desired compound with considerable efficiency and selectivity is a prominent goal of green chemistry. Now a days, designing of ligand free catalytic system with high recyclability points out a major thrust in sustainable organic synthesis [1]. Thus the achievement of successful designed based transition metal nanoparticle broadly improves stability within the solid support, increased chemo/ regioselectivity and reusability for several runs. In this context heterogeneous transition metal nanoparticle having intimate metal surface activation could bring selectivity and efficiency to organic transformation [2]. Huge contribution for green chemical process development has been done by introducing heterogeneous metal nanoparticle in ionic liquid, water and dry media reaction. In this aspect C-C and C-hetero, oxidation and reduction are the most important tools for modern organic synthesis through Suzuki-Miyaura, Heck, Sonogashira, Stille, Ullmann and Buchwald-Hartwig coupling reactions, and are proposed as a point of reference for nano metal catalyst which also fulfill the basic criteria of green chemistry: Prevention, atom ecomony, designing safer chemicals, energy saving, less hazards etc.

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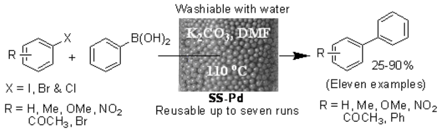
Recently our group have developed a convenient process for in-situ conversion of Pd(II) to Pd(0) and their simultaneous deposition over solid matrix. All the nano and microparticles are well separated by polymer units and due to their spherical shape high catalytic activity has been observed. This air and moisture stable catalytic system has been found to be suitable in different solvents as well as water mediated reactions. Primarily we have applied our catalyst in Suzuki-Miyaura cross coupling [3] and oxidation of benzylalcohols under milder reaction condition [4].

## Application area of our work

### 1. Suzuki-Miyaura cross coupling

Suzuki-Miyaura cross coupling reaction is strategically one of the most important reactions, widely used for the preparation of pharmaceutical, agrochemical, pesticides, valuable natural products and liquid crystalline materials [5]. Due its huge application in industries for important C-C bond formation implies a revolution in society, which led to achievement of noble prize 2010 in chemistry. In palladium catalyzed Suzuki-Miyaura cross coupling reaction, arylboronic acid is all time best fitted coupling partner of aryl halides due to its air and moisture stability as well as functional group compatibility, and introduced a powerful methodological tool through the past era. During the last decades a number of methods have been developed for Suzuki-Miyaura cross coupling reaction, but most of them utilized ligand and harsh reaction conditions [6].

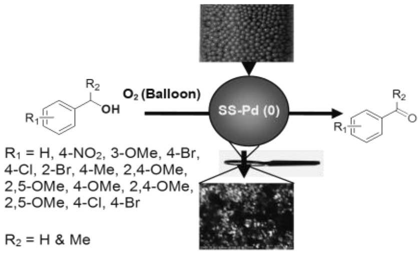
We have reported a facile process for the Suzuki-Miyaura cross coupling reaction of aryl halides (Cl, Br, I) with phenyl boronic acid under ligand free, milder basic conditions using recyclable solid-supported Palladium nano and microparticles as heterogeneous catalyst [3]. Aryl bromides and iodides afforded good to excellent yield of corresponding biaryls irrespective functional group attached with the aromatic ring. Comparatively cheaper and easily available aryl chloride activation for this reaction has been successfully achieved. Aryl chlorides having electron withdrawing functionality gave better yields.



**Scheme 1: Suzuki-Miyaura cross coupling**

### 2. Oxidation reaction

Selective alcohol oxidation is a valuable chemical process in laboratory and industry to obtain aldehyde and ketone. From the prospective of Green Chemistry, environment friendly manufacturing of organic compounds has been considerably reexamined in recent years, and many excellent methodologies have been devised. In this regard, recently we also have reported solid supported palladium catalysed oxidation of benzyl alcohol to aldehydes and ketones under milder conditions using molecular oxygen as green and cheap oxidant giving $H_2O$ as only byproduct. Earlier the reports are mentioned using different bases like $K_2CO_3$, $Na_2CO_3$, and pyridine [7]. But here first time we have reported base free reaction condition for quantitative conversion of benzyl alcohols [4].



**Scheme 2: Oxidation of benzyl alcohol to aldehydes / ketones**

Various benzyl alcohol (primary and secondary) substrates containing electron donating and withdrawing substituents including halogen gave good to excellent yields of corresponding aldehyde and ketone irrespective of their position. The solid supported catalyst was recovered quantitatively by the filtrations from the reaction mixture and was reused for further oxidation reaction after washing. No significant loss of catalytic activity of solid supported palladium was observed up to five runs. The leaching of the Pd metal from the solid surface was almost negligible over the recycles.

***References***:

1. Calo, V.; Nacci, A.; Monopoli, A.; Montingelli, F. *J. Org. Chem.* **2005**, *70*, 6040.

2. For recent reviews on transition - metal NP - catalyzed reactions, see: (a) D. Astruc, F. Lu, J. Ruiz Aranzaes , Angew. Chem. Int. Ed. **2005**, *44*, 7399 ; (b) J. G. De Vries, Dalton Trans. **2006**, *421*; (c) D. Astruc, Inorg. Chem. **2007**, *46*, 1884.

3. Das, P.; Sharma, D.; Shil, A. K.; Kumari, A. Tetrahedron Lett. **2011**, *52*, 1176.

4. Bandana.; Aggarwal, N.; Das, P.; Tetrahedron Lett.**2011**, *52*, 4954.

5. (a) N. Miyaura, A. Suzuki, *Chem. Rev*. **1995**, *95*, 2457; b) J. Hassan, M. SRvignon, C. Gozzi, E Schulz, M. Lemaire, *Chem. Rev*. **2002**, *102*, 1359.

6. (a) T. Ishiyama,, H. Kizaki, T. Hayashi, A. Suzuki, N. Miyaura, *J. Org. Chem.*, **1998**, *63*, 4726; (b) A. R. Martin and Y. Yang, *Acta Chem. Scand.*, **1993,** *47*, 221.

7. (a) Buffin, B.P.; Clarkson, J.P.; Belitz, N.L.; Kundu, A. *J. Mol. Catal. A: Chem.* **2005**, *225*, 111; (b) Pillai, U.R.; Sahle-Demessie, E. *Green Chem.* **2004,** *6*, 161; (c) Caravati, M.; Grunwaldt, J.D.; Baiker, A. *Phys. Chem. Chem. Phys.* **2005**, *7*, 278; (d) Muzart, J. *Tetrahedron* **2003**, *59*, 5789; (e) Caravati, M.; Grunwaldt, J.D.; Baiker, A. *Catal. Today* **2004**, *1*,91.

# Coordination and Organometallic complexes of Rh(III) with α-NaiR(1-alkyl-2-(naphthyl-α-azo)imidazole) ligands

**Dibakar Sardar [#] and Chittaranjan Sinha***

We have been engaged for the last several years to design azo functionalized N-heterocycles and 2-(naphthyl-α/β-azo)imidazole is one of them. Imidazole is very interesting molecule to chemistry and biology [1, 2]. It carries two N-centers of different hardness and can bridge two metal centers. If we block one of the N-centers by alkyl group to synthesize 1-alkyl-2-(napthyl-α/β-azo)imidazole (α/β-NaiR) then molecule may primarily serve as bidentate N-N$^{/}$-chelator. α-NaiR has second advantage that acts as tridentate cyclometalating agent to synthesize palladacycle [3]. This reaction has stimulated us to synthesize organometallics of other platinum group metals. In the present work we have studied the chemistry of Rh(III) complexes with 1-alkyl-2-(napthyl-*α*-azo)imidazole (α-NaiR, R = $CH_3$, $CH_2$-$CH_3$, $CH_2$-Ph).

Reaction of $RhCl_3$ with 1-alkyl-2-(naphthyl-α-azo)imidazole (α-NaiR) has synthesized two different types of complexes in different reaction conditions, one in which the α-NaiR ligand binds with rhodium

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with its two N(azo), N′ (imidazole) donor centre and other gives organorhodium complex in which C-H activation at the naphthyl ring has occurred. All the complexes are characterized by analytical and spectroscopic methods. The structures of both types of complexes are confirmed by single crystal X-ray diffraction study. Density functional theory calculation has also been performed to rationalize the electronic structures and their spectral properties.

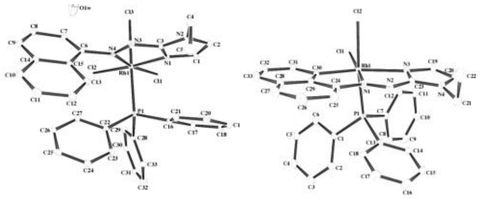

**Fig. 1.** Single crystal X-ray structures of [Rh(α-NaiR- N, N$^{/}$)($PPh_3$)$Cl_3$] (left) and [Rh(α-NaiEt- N, N$^{/}$, C)($PPh_3$)$Cl_2$] (right).

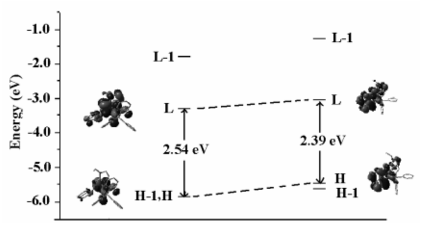

**Fig. 2.** Correlation diagram between [Rh(α-NaiEt-N, N′)($PPh_3$)$Cl_3$] (left) and [Rh(α-NaiEt-N, N′, C)($PPh_3$)$Cl_2$] (right)

***References:***

1. W. Kaim and B. Schwederski, Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, J. Wiley & Sons, Chichester-New York-Brisbane-Toronto Singapore, **1994**.

2. S. J. Lippard, J. M. Berg, Principles of Bioinorganic Chemistry, University Science Books, Mill Valley, CA, **1994**.

3. J. Dinda, D. Das, P. K. Santra, C. Cinha, L. R. Falvello. *J. Org. Met. Chem.* 629, **2001**, 28.

# Computer Simulation : An Approach to Green Chemistry

**Jnanojjal Chanda ***

Green Chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Green Chemistry relies on a set of principles that can be used to design or re-design molecules, materials and chemical transformations to be safer for human health and the environment. The principles of green chemistry provide a framework for scientists to use when designing new materials, products, processes, and systems. The principles focus on sustainable design criteria. Green chemistry embraces this power of design. Computer simulations have a valuable role in this area. It is a powerful tool to study the microscopic behavior of chemical systems, allowing the detailed motions of individual atoms to be observed. The principles of statistical mechanics, which link microscopic motion to macroscopic observables, can be used to process simulated trajectories and estimate measurable properties that can be directly compared with experiments. It can provide essentially exact results for problems in a green way, which would otherwise only be soluble by vigorous experiments. Thus, computer simulation can act as a bridge between models and theoretical predictions

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on the one hand, and between models and the experimental results on the other hand. This is illustrated with a block diagram in Figure 1.Because of this dual role, and the way in which simulations are conducted and analyzed, these techniques are often termed as "Computer Experiment"[1,2]. Today, with the availability of powerful computers and sophisticated methodologies, computer simulation has become an extremely useful technique, and often an important alternative tool to experimental and theoretical approaches in investigating various complex phenomena in chemistry and biology in a green manner. As well as being of academic interest, this type of information is scientifically useful. It may be difficult or impossible to carry out experiments under extremes of temperature and pressure, while a computer simulation of the material, a high-temperature plasma, a nuclear reactor, or a planetary core, would be perfectly feasible. Finally, while the speed of molecular events is itself an experimental difficulty, it presents no hindrance to the simulator. A wide range of physical phenomena, from the molecular scale to the galactic, may be studied using some form of computer simulation.

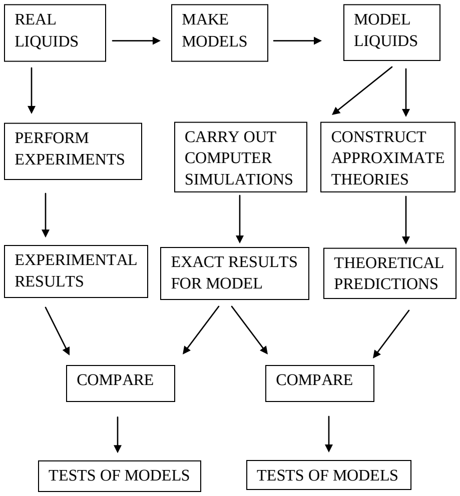

**Fig.1**. The connection between experiment, theory, and computer simulation

***References:***

1. Allen, M.P.; Tildsley, D.J. *Computer Simulation of Liquids*; Clarendon: Oxford, **1987.**
2. Frenkel, D. and Smit, B. *Understanding Molecular Simulation*, Academic Press, London, **1996**.

# Green Chemistry for Undergraduate Students

**Prajnamoy Pal***

Green chemistry is an environment and health conscious revisit of the synthetic chemistry where researchers are engaged to invent, design and develop chemical methods those can diminish or eliminate the use and formation of hazardous substances. It concentrates on waste minimization at source, use of catalysts in place of reagents, using non-toxic reagents, use of renewable resources, improved atom efficiency, use of solvent free or recyclable and use of environmentally benign solvent systems.

There are twelve basic principles of Green Chemistry. Those are:

1) It is better to prevent waste than to treat or clean up waste after it is formed.
2) Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3) Wherever practicable, synthetic methodologies should be designed to use and generate substances that pose little or no toxicity to human health and the environment.
4) Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5) The use of auxiliary substances (e.g. solvents, separation agents *etc*.) should be made unnecessary wherever possible and innocuous when used.

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6) Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7) A raw material feedstock should be renewable rather than depleting whenever technically and economically practical.
8) Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9) Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10) Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11) Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.
12) Substances and the forms of the substance used in chemical reaction should be chosen so as to minimize the potential of chemical accidents, including releases, explosions, and fires.

This presentation has mainly been designed for the students of undergraduate level who are much less conscious about the potential environmental and health hazards of those chemicals used generally in our conventional methods of laboratory experiments. Here we will discuss how some common organic reactions can be nicely achieved through some greener means and what are the potential hazards of the so-called conventional procedures.

**Acetylation of primary amine:**

A primary amine, like aniline, is usually acetylated by acetic anhydride in methylene chloride and pyridine. The last two are very much non-green components in the process. Pyridine is harmful if inhaled, swallowed or absorbed through the skin and might also have minor neurotoxic, genotoxic *(mutagen or carcinogen causing genetic mutation)* and clastogenic *(a form of mutagenesis)* effects. The harmful effects of methylene chloride are also a matter of great concern. The effects are as follows:

*Acute Effects:*

Case studies of methylene chloride poisoning during paint stripping operations have demonstrated that inhalation exposure to extremely high levels can be fatal to humans. Acute inhalation exposure to high levels of methylene chloride in humans has resulted in effects on the central nervous system (CNS) including decreased visual, auditory, and psychomotor functions, but these effects are reversible once exposure ceases. Methylene chloride also irritates the nose and throat at high concentrations. Tests involving acute exposure of animals have shown methylene chloride to have moderate acute toxicity from oral and inhalation exposure.

*Chronic Effects (Noncancerous):*

The major effects from chronic inhalation exposure to methylene chloride in humans are effects on the CNS, such as headaches, dizziness, nausea, and memory loss. Animal studies indicate that the inhalation of methylene chloride causes effects on the liver, kidney, CNS, and cardiovascular system.

*Reproductive / Developmental Effects:*

No studies were located regarding developmental or reproductive effects in humans from inhalation or oral exposure. Animal studies have demonstrated that methylene chloride crosses the placental barrier, and minor skeletal variations and lowered fetal body weights have been noted.

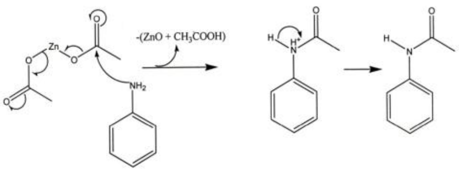
*Cancer Risk:*

Several studies did not report a statistically significant increase in deaths from cancer among workers exposed to methylene chloride. Animal studies have shown an increase in liver and lung cancer and benign mammary gland tumors following inhalation exposure to methylene chloride. EPA considers methylene chloride to be a probable human carcinogen and has ranked it in EPA's Group B2.

Also, the use of acetic anhydride has been banned widely due to its utility in narcotic business.

Interestingly, the same acetylation process can be achieved with as high as 91% yield simply by boiling the amine with acetic acid in presence of Zn-dust, thus avoiding all the hazardous chemicals and minimizing the waste by-products.

The mechanism of the reaction is:

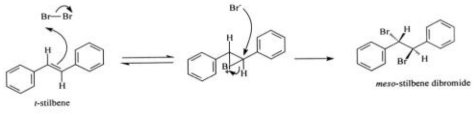


**Halogen addition to carbon-carbon double bond:**

This process is generally carried out with bromine in a chlorinated solvent like methylene chloride etc. and both the chemicals are hazardous in nature. The same conversion can be attained by using the reagent HBr (in water) and 30% $H_2O_2$ (in EtOH) with 71% yield. The process is very much atom efficient with water is the only by-product.

**Mechanism:**

$$2\,HBr + H_2O_2 \xrightarrow[\text{oxidation}]{\textit{in situ}} 2\,H_2O + Br_2$$



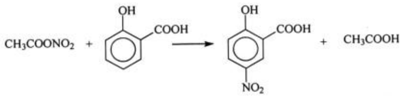
$$5\,NaBr + NaBrO_3 + 6\,CH_3COOH = 3\,Br_2 + 3\,H_2O + 6\,NaOCOCH_3$$

**Aromatic electrophilic substitution reaction:**

A well-known aromatic electrophilic substitution reaction is nitration. In this reaction conc. sulphuric acid and conc. nitric acid used are definitely non-green components. The alternative green procedure is the use of calcium nitrate in acetic acid as reagent. This is a rapid, regioselective and eco-friendly nitration process where the reagents and by-products are useful agrochemicals and environmentally benign.

The mechanism is:

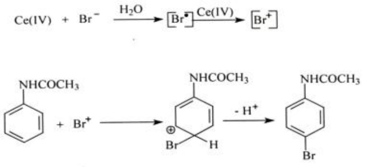
$$Ca(ONO_2)_2 + 2CH_3COOH \longrightarrow 2CH_3COONO_2 + Ca(OH)_2$$



$$Ca(OH)_2 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + 2H_2O$$

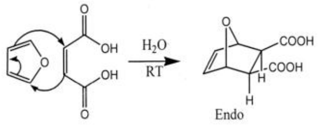
Bromination of acetanilide is another example of aromatic electrophilic substitution reaction where liquid bromine in glacial acetic acid is used as brominating agent. Liquid bromine itself is a non-green component of this reaction. This reaction can alternatively been carried out in green environment using ceric ammonium nitrate (CAN) with KBr (in $H_2O$/EtOH) with as high as 85% yield.

The mechanism of the reaction is as follows:



Reaction between furan and maleic acid is a typical **Diels-Alder reaction [(4+2) cycloaddition]** which is conventionally carried out by refluxing the system in benzene (a non-green component). But with green approach the reaction can be effectively carried out at room temperature in water which is a 100% atom efficient process with 80% yield.

The mechanism is:



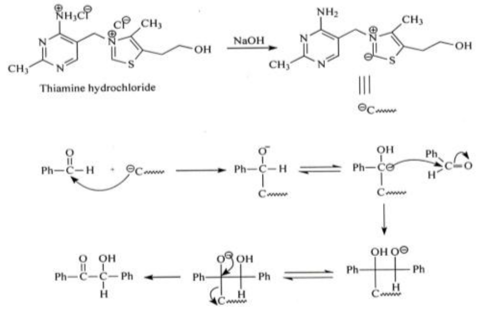
**Benzoin condensation:**

This is a well-known condensation reaction carried out conventionally with sodium cyanide in presence of aqueous ethanol. But with its highly poisonous nature sodium cyanide is surely a non-green component.

*[CYANIDE POISONING: Cyanide makes the cells of an organism unable to use oxygen, primarily through the inhibition of cytochrome c oxidase. Inhalation of high of cyanide causes a coma with seizures, apnea, and cardiac arrest, with death following in a matter of minutes. At lower doses, loss of consciousness may be preceded by general weakness, giddiness, headaches, vertigo, confusion, and perceived difficulty in breathing. At the first stages of unconsciousness, breathing is often sufficient or even rapid, although the state of the victim progresses towards a deep coma, sometimes accompanied by pulmonary edema, and finally cardiac arrest. Skin color goes pink from cyanide-hemoglobin complexes. A fatal dose for humans can be as low as 1.5 mg/kg body weight. Blood cyanide concentrations may be measured as a means of confirming the diagnosis in hospitalized patients or to assist in the forensic investigation of a criminal poisoning. Cyanide toxicity can occur following ingestion of amygdalin (found in almonds and apricot kernels and marketed as an alternative cancer cure), prolonged administration of nitroprusside, and after exposure to gases produced by the combustion of synthetic materials]*.

The same reaction can efficiently be carried out with thiamine hydrochloride in a totally green environment.

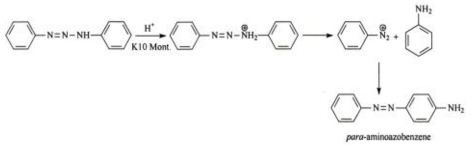
**Mechanism:**



**Conversion of diazoaminobenzene to p-aminobenzene:**

This conversion is typically done by with anilinium hydrochloride in acetic acid. But with the use of K10 montmorillonite [a phyllosilicate group of minerals forming a clay, $[(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O]$] the conversion can be achieved in an eco-friendly pathway.

**Mechanism:**



Similarly, many other organic reactions can be achieved with high efficiency following eco-friendly green methods avoiding health hazards. Some of those reactions are base-catalyzed aldol condensation, benzil-benzilic acid rearrangement, pinacol-pinacolone rearrangement, some oxidation reactions, microwave-assisted ammonium formate-mediated Knoevenagel reaction (an example of solvent-free reaction), synthesis of biodiesel etc.

Chemistry is the very core of our life, of our livelihood. Advancement of chemistry is very much an intrinsic demand for all of us, but we must remain extremely conscious so that the advancement can never bring annihilation in disguise. And for this, we must cultivate chemistry with as much eco-friendly approach as possible with utmost eradication of potential health hazards. At this point lays the very significance of Green Chemistry. We must offer our future generations a nice green environment.

***Reference:***

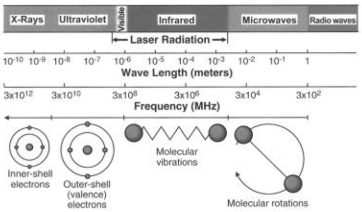
Monograph on Green Chemistry Laboratory Experiment, DST, Govt. of India, and the references therein.

# Some Microwave-Assisted Organic Synthesis

**Moumita Sen Sarma***

Microwave radiation is a type of electromagnetic radiation that lies between infrared radiation and radio waves with wavelengths of 1mm to 1m and corresponding frequencies between 0.3 to 300 GHz.

*The electromagnetic spectrum*



In organic chemistry microwave technology has been inducted only since the mid-1980s. Heating in most organic reactions are traditionally done by some conventional heat transfer equipments like oil bath, sand bath, water bath and heating jackets. The drawbacks of all these techniques include the processes are rather slow and a temperature gradient may be developed within samples and also local overheating may with all probability leads to decomposition of substrate, product and/or reagent molecules. On the other hand, in microwave dielectric heating the microwave energy is remotely introduced in the chemical reactor and the

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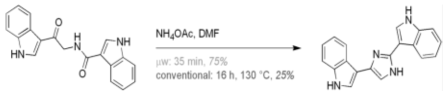
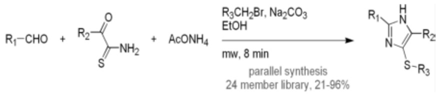
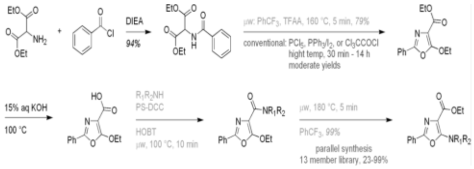
reaction vessel gets direct access of the energy source. The microwave radiation heats the reactants and solvent and not the reaction vessel itself. By designing the apparatus suitably, a uniform increase in temperature can be maintained which leads to less by-products or products by decomposition.

Some recent applications of microwave-assisted organic synthesis are:

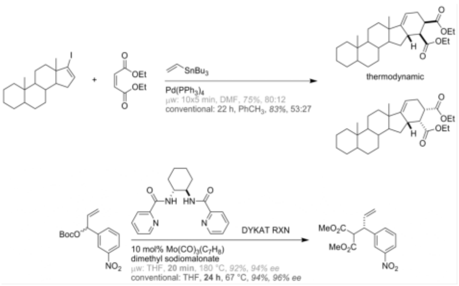
**Heterocycles**



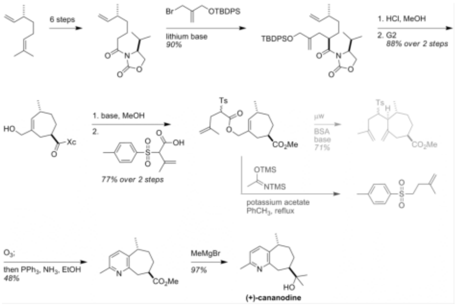




## Organometallic reactions



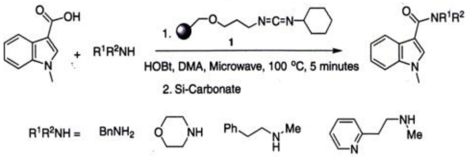
## Rearrangements



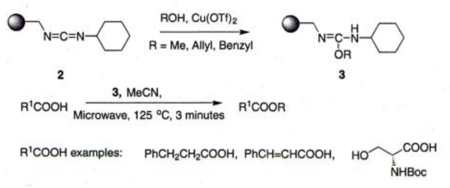
## Radical initiation

The use of polymer-supported reagents and scavengers is a powerful technique for expedited synthesis and purification. By using polymer-supported reagents and scavengers, excess reagents and by-products can be selectively removed by a simple filtration rather than liquid-liquid extraction and chromatographic purification. In addition, polymer-supported reagents offer further advantages that include reaction of active intermediates by "catch-and-release", selectivity and immobilization of toxic intermediates.

## Amide synthesis using PS-Carbodiimide



**Synthesis of carboxylic esters using Polymer-supported isoureas**



Thus, microwave assisted organic synthesis has become an important tool to chemists for rapid, efficient and eco-friendly organic synthesis.

***References:***

1. Lidstrom P, Tierney J, Wathey B, Westman J. Microwave-assisted Organic Synthesis: A Review. *Tetrahedron*, **2001,** 57, 9225-9283.
2. Jacobs DL. Microwave-assisted organic Synthesis. *Crimmins Group Meeting*, **10/11/2006**.

# Green Chemistry – UG Level

**Rana Karmakar***

*Green /* Sustainable / Environmentally benign Chemistry ***are the design, development and implementation of chemical products and processes that reduce or eliminate the use of substances hazardous to human health and the environment.***

According to Daryle Busch, President of ACS, ***"Green chemistry represents the pillars that hold up our sustainable future. It is imperative to teach the value of green chemistry to tomorrow's chemists."*** [1]

Simply we may say that Green chemistry deals with the processes that are nature friendly and the products are readily degradable so that it can fulfill our sustainability - "Meeting the needs of the present generation without compromising the ability of future generations to meet their needs”. The primary intention is to minimize the energy / resource uses that will help to enhance the efficiency, avoids large waste materials and also utilize renewable resources. A few steps that can be helpful to achieve the targets are:

- **Controlling the uses of conventional volatile organic solvents**
- **Solvent free synthesis**
- **Replacing volatile solvents by alternatives (Room temperature ionic liquids, Water, Super critical carbon dioxide etc.)**
- **Introducing biodegradable polymers**

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- **Minimization of solid waste materials**
- **Making lead and mercury free electronics components**
- **Enhancement of atom economy**
  (How many of the atoms of the reactant are incorporated into the final product and how many are wasted)

### *Role of Green Chemistry*

The war started from early 1990s by incorporating 'The Pollution Prevention Act', in 1996, Presidential Green Chemistry Challenge awards and so on. Finally a journal "Green Chemistry" itself started publishing from the year 1999. The approaches made greener for the preparation of chlorinated solvents, biodegradable polymers, replacing different volatile organic solvents (VOCs) by water, room temperature ionic liquids or supercritical carbon dioxide. New synthetic process is adopted for preparation of Ibuprofen and Zoloft, production of different integrated circuits and removing arsenic and chromate from pressure treated wood. Many environmentally benign pesticides are getting synthesized, metallic lead is removed from automobile fuel and paints, Trans fats in oils is lowered. On the way in 2005, The Royal Swedish Academy of Sciences has decided to award the **Nobel Prize** jointly to Yves Chauvin, Robert H. Grubbs and Richard R. Schrock for their work **- "The development of the metathesis method in organic synthesis"**.

### *Greening the Chemistry Curriculum*

A new approach is already adopted globally to insert green chemistry in the mainstream chemistry courses and for these purpose faculties are employed who can teaches these courses and develop modules on green chemistry related topics. Efforts are given to distribute the knowledge through books, journals and web so that a social awareness can be enhanced from all sides.

In our country we are also exploring research and development to carry out chemical reactions by avoiding conventional solvents and therefore emphasis are given to synthesize different green solvents and use it as an alternatives. In the year 2004, Department of Science and Technology (DST) has formed "Green Chemistry Task Force Committee" to emphasize safe green laboratory experiments. Various seminars and workshops are organized throughout the country for promoting social awareness. Environmental studies are made as a compulsory subject both in school and college levels by the order of Supreme Court, India. The University of Calcutta has started a short term project work in the under graduate level curriculum so that a student can also enrich himself through some practical knowledge along with class room studies.

### *Green Guidelines in the Chemistry Laboratory*

In the college level where only simple chemical processes are performed, still we should maintain the following rules that not only make our environment clean but also avoid unnecessary health hazards.

- Our laboratory should be in HEALTHY condition so that we can breathe inside it.
- Try to do all experiments in the laboratory in semi-micro or micro-scale so that wastage of chemical is minimized.

- While using concentrated acids and licker ammonia uses of 'Fume cup board with proper filter' should be made compulsory to avoid unnecessary health hazards.
- For the detection of radicals "Spot-tests" should be preferred.
- Uses of eco-friendly and low cost reagents may cut down our total budget.
- Water soluble alcohols should be given preference rather than volatile organic solvents like ether, benzene, $CCl_4$ etc.
- Modified Experiments is preferred where high pressure, high temperature and long duration reactions are avoided.
- TLC should be the method of choice for determining purity of the compound.
- One can use ethyl chloroformate as a substitute for $PCl_5$/ $SOCl_2$. The acid is converted to anhydride which can be used for the same purpose.
- A saturated solution of $H_2S$ is always better instead of direct using the gas from Kipp's apparatus.
- Phenol – water phase diagram experiment must be replaced.

## Green methods for some basic experiments in the UG level:

### ✶ *Organic qualitative analysis for detection of special elements - N, S, and halogens*

A little organic sample is added on fused metallic sodium taken in a fusion tube and after heating strongly it is dipped into distilled water taken in a mortar and filtered. The filtrate is then used for Lassaigne's test.

***Alternatives:***

**Use of zinc and sodium carbonate instead of metallic sodium** [3a]

The same organic sample (~50 mg) is mixed with Zn dust (~200 mg) and $Na_2CO_3$ (300 mg). The mixture is taken in a fusion tube and heated gently for few minutes and finally kept at red hot condition for more than 2 minutes. The fusion tube is then plunged into 5 ml distil water taken in a mortar, ground well and filtered. The filtrate is used for Lassaigne's test as usual.

***Advantages:***

- Replacement of hazardous sodium metal, which is usually difficult to handle in hygroscopic weather especially in rainy season.
- Sodium is highly corrosive and incomplete burn may catch fire and explosion occurs in presence of water but zinc and sodium carbonate mixture is devoid of such problems.
- Zn – $Na_2CO_3$ mixture is rather easy for long term preservation compared to metallic sodium**.**

### ✶ *Preparation of Carboxylic acid derivative*

***Conventional procedure:***

Carboxylic acid sample is reacted with corrosive and volatile $PCl_5$ / $SOCl_2$ to make acid chloride intermediate and from this corresponding amide or anilide derivatives are produced.

***Greener approach:***

### Preparation of N-Benzyl Benzamide from Benzoic acid [3b]

1.2 g of benzoic acid and 1.5 ml triethylamine are mixed with 50 ml diethyl ether taken in a conical flask at room temperature. In this mixture 0.8 ml of methyl chloroformate is added drop by drop with vigorous stirring at room temperature for 2 minutes. The mixture is then filtered through a buchner funnel and the precipitate was washed with diethyl ether (~10 ml). 1.1 ml of benzylamine is added to this combined ether layer at room temperature. Diethyl ether was allowed to evaporate over water bath. This viscous residue is cooled in crushed ice and a white precipitate of N-benzyl benzamide is formed which is then filtered and finally air-dried. The chemical reaction is shown in Fig. 1.

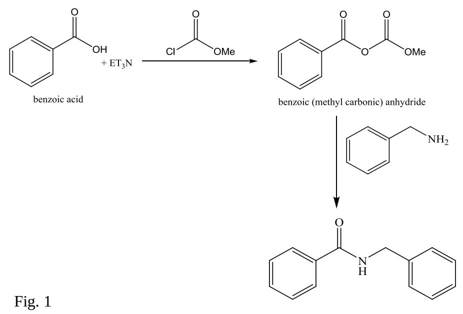


Fig. 1

### ✶ Bromo derivative of Acetanilide:

***Conventional Procedure:***

Drop wise addition of bromine to acetanilide in presence of glacial acetic acid produces p- bromo acetanilide derivative.

***Alternative Green Way:*** [2]

1 g of acetanilide dissolved in 15 - 20 ml ethanol taken in a round bottomed flask and an aqueous mixture of 1 g KBr and 6 g ceric ammonium nitrate (CAN) is added drop wise to it. After the addition is complete the reaction mixture is stirred for about 10 minutes at room temperature until white crystals starts separating. The crystals are poured in ice-water and filtered. Finally it is dried under pressure.

***Green Context:***

- Corrosive and volatile liquid bromine is replaced with a novel brominating agent.
- Water is used as solvents instead of glacial acetic acid.
- Enhanced reaction rate.

### ✶ Separation of Cu$^{+2}$ and Cd$^{+2}$ in group II:

***Conventional Procedure:***

Deadly poisonous aqueous potassium cyanide solution is used.

***Alternative Way:*** [3c]

The greener procedure for this separation is schematically shown in Fig. 2, where uses of potassium cyanide can be avoided.

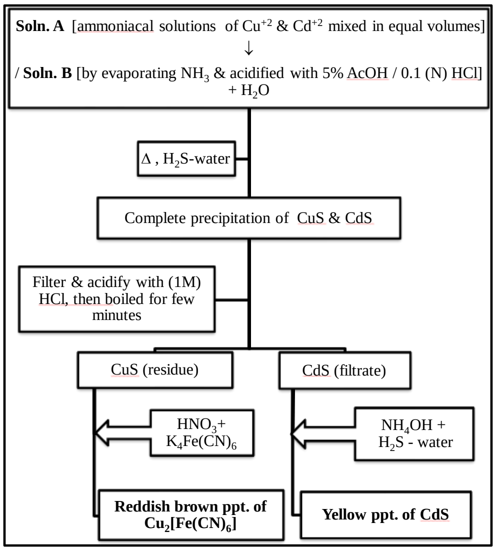


Fig. 2. Separation of $Cu^{+2}$ and $Cd^{+2}$ radicals from a mixed solution.

### ✶ *Reduction of aqueous $Fe^{+3}$ to $Fe^{+2}$*

***Non Green Procedure:***

25 ml of aqueous $Fe^{+3}$ solution is taken in a 250 ml conical flask and 5 ml conc. HCl is added to it so that pH of the solution should be ~5-

6(M). The mixture is then heated to 80–90$^0$C temperature. Now aqueous $SnCl_2$ solution is added drop wise until the yellow colour of the solution is just disappear. The conical is cooled under tap water and slowly 10 ml 5% $HgCl_2$ solution is added to it. A silky white precipitate is appeared then the mixture is titrated with standard potassium dichromate solution.

$2\ FeCl_3 + SnCl_2 = 2\ FeCl_2 + SnCl_4$

$2\ HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$

### Greener approach by replacing Mercury compound with Al foils:

In 25 ml of aqueous $Fe^{+3}$ solution taken in a 250 ml conical flask, 5 ml conc. HCl and 3-4 pieces of Aluminum foil are added. The mixture is then boiled until the yellow colour of $Fe^{+3}$ are completely disappearing. It is cooled and 150 ml water is added to it. After addition of 2g solid $NH_4HF_2$ or 5ml syrupy $H_3PO_4$, the mixture is titrated against standard potassium dichromate solution.

$2\ FeCl_3 + Al = 2\ FeCl_2 + AlCl_4$

### *Acknowledgement:*

University Grant Commission for funding the seminar.

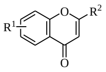
### *References:*

1. Daryle Busch, President ACS, June 26, 2000, "Color Me Green" *Chem. Eng. News.* **2000**, *78* (28), 49-55.
2. P. F.Schatz, *Journal of Chemical Education**. 1996,*** 173, 267.
3. (a-c) Monograph on Green Chemistry Laboratory Experiment, *DST*, 54 - 62.

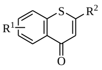
# An Innovative Green methodology for Synthesis of Benzylidene and Cinnamylidene Derivatives of Some Homocyclic and Heterocyclic Ketones

**Tapas Kumar Mandal***

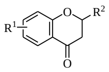
Both natural and synthetic chromone derivatives (*e.g.*, **1**) are known to show important biological activities[1,2]. Thiochromones (**2**) are mostly synthetic compounds and some of their derivatives are reported to show medicinal properties[3,4]. Current literature shows that there has been a growing trend towards synthesis of heterocycles containing these two ring systems[5]. A survey of interesting biological activities of these compounds, newer synthetic routes leading to them and their useful transformations are very much important**.** The same aspects of the corresponding reduced systems, *viz.*, chroman-4-ones (**3**) and 1-thiochroman-4-ones (**4**) are also important. The last group of compounds possesses a ketomethylene moiety. Condensation of aromatic aldehydes at this moiety as shown below appears to be an entry point for synthesis of complex molecules containing chromone and thiochromone units.



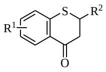
**1**



**2**



**3**



**4**

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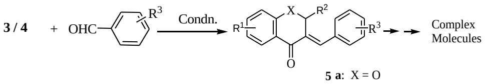
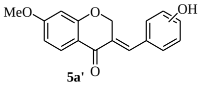
In this connection it may be mentioned that *E*-3- benzylidenechroman-4-ones (**5a**) and structurally related compounds, commonly known as homoisoflavonoids, occur in the plant kingdom and many of them show interesting biological activities.

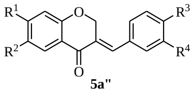


**5 a**: X = O
**b**: X = S

To mention a few, *E*-3-benzylidenechromanones of the types **5a′** and **5a″** are known to show antioxidant (protect Linolenic Acid and DNA against oxidation)[6] and antibacterial & antifungal[7] activities, respectively, 3-benzylchromones (**6**) (endocyclic isomer of **5a**) antioxidant activities[8], and the related tetracyclic compounds such as brazilein (**7**) and brazilin (**8**) anti-inflamatory and cytotoxic activities,[9]. The aforesaid condensation has been reported to be performed in a number of ways.

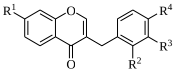


**5a'**



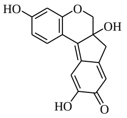
**5a"**

$R^1 = R^2 = R^4 = OMe, R^3 = H$
$R^1 = R^4 = R^3 = OMe, R^2 = H$
$R^1 = OH, R^2 = H, R^3 = H, R^4 = OMe$

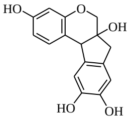


**6**

$R^1 = R^2 = R^3 = H, R^4 = Cl$
$R^1 = OBz, R^2 = R^3 = H, R^4 = OCH_3$
$R^1 = R^3 = R^4 = OCH_3, R^2 = H$
$R^1 = OH, R^2 = R^3 = H, R^4 = OCH_3$
$R^1 = OH, R^3 = H, R^2 = R^4 = OCH_3$



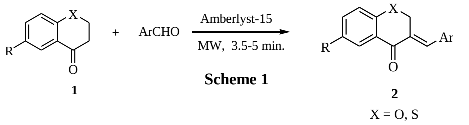
**7**
**Brazilein**



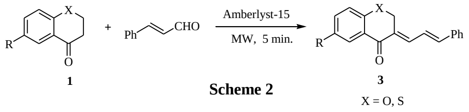
**8**
**Brazilin**

The initial methods were base-catalyzed processes[10], and subsequently, acid-catalyzed methods have also been developed[11]. Modifications like condensation using acetic anhydride[12] or piperidine[13] have also been reported. The acid-catalyzed processes are sometimes two-step processes, the first step giving an aldol which is required to be dehydrated subsequently[14].

Amberlyst-15 is a sulphonated polystyrene resin[15] that has been used for a large number of transformations promoted by strong acids. Microwave irradiation is an efficient and environmentally benign method to activate various organic transformations to afford products in higher yields in shorter reaction periods. Among the MW-assisted reactions, solvent free processes are of particular interest and importance in view of their simplicity, tunability and ease of work-up[16]. Synthesis of *E*-3-arylidenechromanones and *E*-3-arylidenethiochromanones with different aromatic aldehydes and cinnamaldehyde has been done by using Amberlyst-15 as catalyst under microwave irradiation in solvent free condition (Schemes-1 & 2) and the process is environmentally benign and green method.



**Scheme 1**



**Scheme 2**

***References:***

1. (a) J. W. McClure, J. B. Harborne, T. J. Mabry and H (Eds.) Mabry, The Flavonoids, Chapman and Hall: London, 1975, p. 970, (b) G. Atassi, P. Briet, J. P. Berthelon and F. Collonges, *J. Med. Chem.*,**1985**, *20*, 393. (c) Jr. E. Middleton, C. Kandaswami and J. B (Eds.) Harborne, *The Flavonoids Advances in Research since 1986,* Chapman and Hall: London, 1994, p. 619, (d) J. Bruneton, *Pharmacognosy, Phytochemistry and Medicinal Plants*, English Translation by Hatton C K, Lavoisier Publishing, Paris, 1995, p. 265, (e) J. B. Harborne and C. A. Williams, *Phytochemistry*, **2000**, *55*, 481.

2. (a) A. Gupta, A. Dwivedy, G. Keshri, R. Sharma, A. K. Balapure, M. M. Singh. and Ray S, *Bioorg. Med. Chem. Lett.*, **2006**, *16*, 6006, (b) A. Foroumadi, A. Samzadeh-Kermann, S. Emami, G. Dehghan, M. Sorkhi, F. Arobsorkhi, M. R. Heidari, M. Abdollahi and A. Shafiee, *Bioorg. Med. Chem. Lett.*, **2007**, *17*, 6764.

3. (a) A. R. Katrizky and A. J. Boulton, *J. Adv. Heterocycl. Chem*., **1975**, *18*, 76, (b) G. W. Buston, E. Gobe, L. Huges, F. Lee, L. Prasad and K. U. Ingold, *J. Amer. Chem. Soc*., **1985**, *107*, 7053.

4. (a) H.-K. Wang, K. F. Bastow, L. M. Cosentino and K.-H. Lee, *J. Med. Chem.*,**1996**, *39*, 1975, (b) Y. Liu, W. Luo, L. Sun and C. Guo, *Drug Disco. Ther*., **2008**, *2*, 216, (c) A. M. Ribeiro, A. R. Bertoti and T. C. Netto-Ferreira, *J. Braz. Chem. Soc.*, **2010**, *21*, 1071.

5. (a) C. K. Ghosh and A. Patra, *J. Het. Chem.*,**2008**, *45*, 1529, (b) M. A. Ibrahim, T. E. Ali, Y. A. Alnamer and Y. A. Gaber, *Arkivoc*, **2010** (i), *98*, (c) N.-G. Li, Z.-H. Shi, Y.-P. Tang, H.-Y. Ma, J.-P. Yang, B.-Q. Li, Z.-J. Wang, S.-L. Song and J.-A. Duan, *J. Het. Chem.*, **2010**, *47*, 785, (d) W. Wang, H. Li, J. Wang and L. Zu, *J. Am. Chem. Soc*., **2006**, *128*, 10354.

6. Y.-F. Li, Z.- Q. Liu and X.-Y. Luo, *J. Agric. Food Chem*., **2010**, *58*, 4126, and references cited therein.

7. B. Das, P. Thirupathi, B. Ravikanth, R. A. Kumar, A. V. S. Sarma and S. J. Basha, *Chem. Pharm. Bull.*, **2009**, *57*, 1139, and references cited therein.

8. V. M. Rao, G. L. V. Damu, D. Sudhakar, V. Siddaiah, C. V. Rao, *ARKIVOC*, **2009**(xi), 285, and references cited therein.

9. C.-T. Yen, K. Wakagawa-Goto, T.-L. Hwang, P.-C. Wa, S. L. Morris-Natschke, W.-C. Lai, K. F. Baslow, F.-R. Chang, Y.-C. Wu and K.-H. Lee, *Bioorg. Med. Chem. Lett.*, **2010**, *20*, 1037.

10. (a) P. Pfeiffer and H. J. Emmer, *Chem. Ber*. **1920**, *53*, 945, (b) P. Pfeiffer, H. Oberlin and E. Konermann, *Chem. Ber*., **1925**, *58*, 1946.

11. (a) F. Arndt and G. Kallner, *Chem. Ber*. **1924**, *57*, 202, (b) O. Dann and H.Hofmann, *Chem. Ber*. **1962**, *95*, 1446, (c) O. Dann and H. Hofmann, *Chem. Ber*. **1965**, *98*, 1498, (d) D. Evans, and M. Lockbart, *J. Chem. Soc*. 1966, 711, (e) P. Pfeiffer, E. Breitb and H. Hoyer, *J. Prakt. Chem*. **1931**, *31*, 129, (f) P. Pfeiffer and E. Dobring, *Chem. Ber.* **1938**, *71*, 279, (g) P. Pfeiffer, K. Grimm and H. Schmidt, *Liebigs Ann. Chem*. **1949**, *564*, 208, (h) G. Wagner, C. Garbe, H. Vieweg, M. Brunn and A. Dittrich, *Pharmazie*, **1979**, *34*, 55, (i) G. Wagner, H. Horn, B. Eppner and H. Kuhmstedt, *Pharmazie*, **1979**, *34*, 56.

12. (a) L. Farkas, A. Gottsegen and M. Nogradi, *Tetrahedron Lett*., **1968**, *4099*, (b) L. Farkas, A. Gottsegen and M. Nogradi, *Tetrahedron*, **1970**, *26*, 2787, (c) L. Farkas, A. Gottsegen, M. Nogradi and J. Strelisky, *Tetrahedron*, **1971**, *27*, 5049.

13. (a) A. Levai and E. H. Hetey, *Pharmazie*, **1978**, ***33***, 378, (b) A. Levai and J. B. Schag, *Pharmazie,* **1979**, *34*, 749, (c) A. Levai, A. Szollosy and G. Toth, *Acta Chin. Hung*. **1991,** *128*, 359, (d) A. Levai, *Arkivoc*, **2004**, (vii**),** 15.

14. A. Chatterjee, L. N. Dutta and S. K. Chatterjee, *Indian J. Chem.*, **1980**, *19B*, 955.

15. Amberlyst-15 Synthetic Resin Catalyst, Technical Bulletin—Fluid Process Chemicals, Rohm and Haas Company, Inc., Philadelphia, PA, **1978.**

16. *Selected reviews*: (a) S. Caddick, *Tetrahedron* **1995**, *51*, 10403, (b) C. R. Strauss and R. W. Trainor, *Aust. J. Chem.* **1995**, *48*, 1665, (c) S. A. Galema, *Chem. Soc. Rev.* **1997**, *26*, 233, (d) A. Loupy, A. Petit, J. Hamelin , F. Texier-Boullet, P. Jacqualt and D. Mathe, *Synthesis*, **1998**, 1213, (e) R. S. Varma, *Green Chemistry* **1999**, 43, (f) R. S. Varma, *Pure Appl. Chem.* **2001**,*73***,** 193, (g) R. S. Varma, *Organic Synthesis using Microwaves and Supported Reagents.* In: Microwaves in Organic Synthesis, A. Loupy, Ed., Wiley-VCH: Weinheim, **2002**, 181, (h) R. S. Varma, *Advances in Green Chemistry: Chemical Synthesis using Microwave Irradiation.* Astra Zeneca Research Foundation India: Bangalore, India, **2002** (free copy available from:azrefi@astrazeneca.com). (i) R S,Varma, *Tetrahedron*, **2002**, *58*, 1235.