

GREEN AND SUSTAINABLE CHEMISTRY

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I. INTRODUCTION

Increase in global warming and pollution due to chemicals increase the demand for Green and sustainable chemistry. There is a need for more environmentally benign process in chemical industry, which become known as ‘green chemistry or sustainable chemistry’.¹⁻

³ In traditional, the concept of efficiency is basically focus on money, time and yield of product but green chemistry shift this paradigm to eliminating waste at source and avoid the use of toxic/ hazardous chemicals and/ or solvents.

Green chemistry term first time used by Anastas USEPA (US Environmental Protection Agency) in 1993 and USEPA officially accepted the ‘US Green Chemistry Program’.³ In 1999, Royal Society of Chemistry inaugurated the journal ‘Green chemistry’, which define green chemistry as “Green chemistry efficiently utilizes (preferably renewable) raw materials, eliminate waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products”.⁴ In 1998, Anastas gave the principal and guidelines of green chemistry. The concept of green chemistry embodied in 12 Principals of Green Chemistry, which are given below:

1. Waste prevention instead of remediation
2. Atom efficiency
3. Less hazardous/toxic chemicals
4. Safer products by design
5. Innocuous solvents and auxiliaries
6. Energy efficient by design
7. Preferably renewable raw materials
8. Shorter synthesis (avoid derivatization)
9. Catalytic rather than stoichiometric reagents
10. Design products for degaradation
11. Analytical methodologies for pollution prevention
12. Inherently safer processes

Green chemistry is basically the design of products and processes that minimize or eliminate the use or generation of hazardous chemicals. Green chemistry applicable to complete life cycle of a chemical product including design, manufacture, use and disposal. According to OECD (Organization for Economic Co-operation and Development) *Sustainable chemistry encompasses the design, manufacture and use of efficient, effective, safe and more environmentally benign products and processes.*⁵

E-factor and atom efficiency are two powerful tools to measure environmental acceptability of a chemical reaction.^{6,7} E-factor is calculated by mass ratio of waste to desired product while atom efficiency is defined by dividing the molecular weight of product by the molecular weight of all the reactants. E-factor includes solvent loss and the chemical loss during work-up. E-factor is additive for individual steps and calculated for single and multistep processes. Zero value of E-factor indicates that the waste generated in the reaction is very less and reaction is greener and sustainable. E-factor of some reactions are given in Table. 1.

Table 1: E-factor of some industry

Industry Segment	Product tonnage	kg waste/ kg product
Oil refining	10^6 - 10^8	<0.1
Bulk chemicals	10^4 - 10^6	<1-5
Fine chemicals	10^2 - 10^4	5-50+
Pharmaceuticals	10 - 10^3	25-100+

In 1999, Hudlicky have proposed the Effective Mass Yield, which use percentage of product of all the materials used in the synthesis.⁸ It do not includes the chemicals which are environmentally benign like NaCl, acetic acid but this is very questionable because their impact on environment is depends on volume of chemical. Term atom efficiency or atom economy is firstly used by Trost and it is

valuable method for calculation of amount of waste generated during a chemical reaction.⁹ Atom efficiency is defined as the molecular weights of the product to the sum of molecular weight of all the reactants in the reaction involved. The oxidation of secondary alcohol using chromic acid and molecular oxygen given in figure 1.

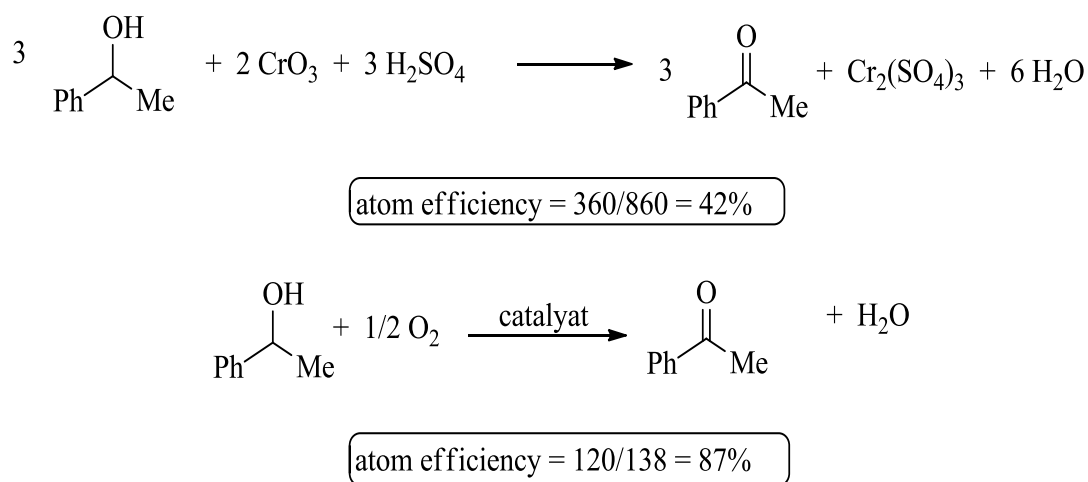


Figure 1: Atom efficiency comparison of two oxidation reactions.

E-factor is a theoretical number and in E-factor it is assumed that all the molecule yielded 100% yield but this will not happened in case of stoichiometric amount of reagent is used. E-factor can be derived from atom efficiency, if atom efficiency is 33.3% than E-factor will be 2 ($66.6/33.3$). Stoichiometric inorganic reagents always reduce the E-factor value while catalytic amount of reagent always increase the E-factor value. Yield and selectivity are two ways by which efficiency of a chemical reaction can be defined but these don't give much information about the waste produced in a chemical reaction. Apart from this, atom economy is a quantitative measure to calculate how much atom is required to give desired product.¹⁰ The atom economy can be understand by oxidation of alcohol to a carboxylic acid with chromium (VI) as oxidizing agent. Table 2 shows that only carbon atom likely to approach 100% atom efficiency and it also depends upon reaction selectivity.¹¹

Table 2: Atom accounts for a typical partial oxidation reaction using chromate

Element	Fate	Atom utilization
C	Product(s)	Up to 100%
H	Product(s) +waste acid	<100%
Cr	Chromium waste	0%
Na	Salt waste	0%
S	Salt waste (after acid neutralization)	0%
O	Product(s) + waste	<<100%

In this chapter we will discuss designing the novel methodologies, which are in recent trends to minimize or eliminate hazardous chemicals. In this chapter, we also discuss solid support acid base catalysis, oxidation and reduction catalysis, electrochemical, grinding and sonication based green methodologies.

Solid Acid-Base Mediated Synthesis: The major source of waste are mineral acids like HF, HCl and H₂SO₄ in a chemical industry because they cannot be recycled and ends up in hydrolytic workup and some are corrosive in nature. Their replacement with recyclable solid acids such as zeolites, acidic clays and derived mineral acids have many advantages.¹²⁻¹⁴ All the reactions such as esterification, condensation, nitration, Friedel-Craft alkylation and sulfonylation carried out using solid acid catalysis. In 2006, Takagaki and co-workers have reported the novel solid acid catalyzed esterification of fatty acid.¹⁵ Using solid acid reduce the E-factor and it can be recovered. The carbon material prepared from D-glucose act as solid acid catalyst. The amorphous carbon sulfonic acid is a bronsted acid catalyst for the conversion of biomass and cellulose saccharification have reported by Hara *et. al.*¹⁶ Graphene sulfonic acid can be synthesized by treating grapheme with *para*-diazophenylsulfonic acid in presence of H₃PO₂ (Figure 2).

Graphene sulfonic acid used as a catalyst in various heterocyclic synthesis reactions like pyrido[2,3-*d*]pyrimidine, benzimidazole etc.¹⁷ Pyrido[2,3-*d*]pyrimidine synthesized by one pot multicomponent reaction between 4-aminocoumarin, thiobarbituric acid and aromatic aldehyde at in presence of graphene sulfonic acid as reusable catalyst. Similarly, zeolite act as the catalyst in acetylation reaction. The reaction between anisole with acetic anhydride to give para methoxyacetophenone. In many acetylation reactions, zeolite act as an alternate to AlCl_3 because AlCl_3 reacts with water during workup and cannot get isolated. The comparison between homogenous catalyst catalyzed reaction and heterogeneous catalyst reaction given in Table 3.¹⁸ Table clearly show that the heterogeneous catalyst catalyzed reactions produces only 0.035 Kg of effluents per Kg while homogeneous catalyst catalyzed reaction produces 4.5 Kg clearly shows that zeolite mediated reaction are more greener and environmentally benign.

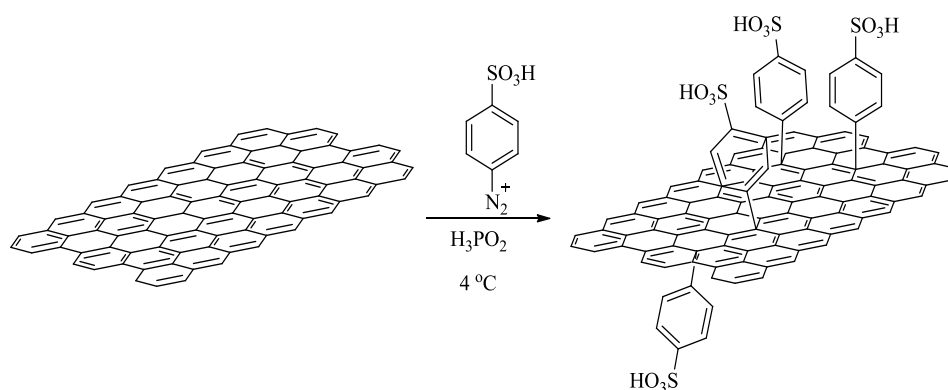


Figure 2: Synthesis of graphene sulfonic acid (solid recyclable catalyst).

Table 3: Heterogeneous v/s homogeneous catalysis

Homogeneous	Heterogeneous
$\text{AlCl}_3 > 1$ equiv.	Catalytic and reusable
Solvent	No-solvent
Hydrolysis of products	No water necessary
Phase separation	-

Distillation of organic phase	Distillation of organic phase
Solvent recycle	-
85-95% yield	> 95% yield with higher purity
4.5 Kg aqueous effluents per Kg	0.035 Kg aqueous effluents per Kg
12 operations	3 operations

Oxidation and Reduction Methods: Molecular hydrogen act as clean and green raw material for catalytic hydrogenation, which are 100% efficient and exhibit tremendous chemo-, region- and enantioselectivity.¹⁹ As discussed above, heterogeneous reduction reaction are much greener because all the metals (Ni, Pd, Pt, etc) used in reduction reaction are catalyst and reusable up to 5 cycles. In 2001, Nobel prize in chemistry given to W.S. Knowles, R. Noyori and K.B. Sharpless for asymmetric catalytic oxidation of allylic alcohols to their epoxide (Figure 3).²⁰

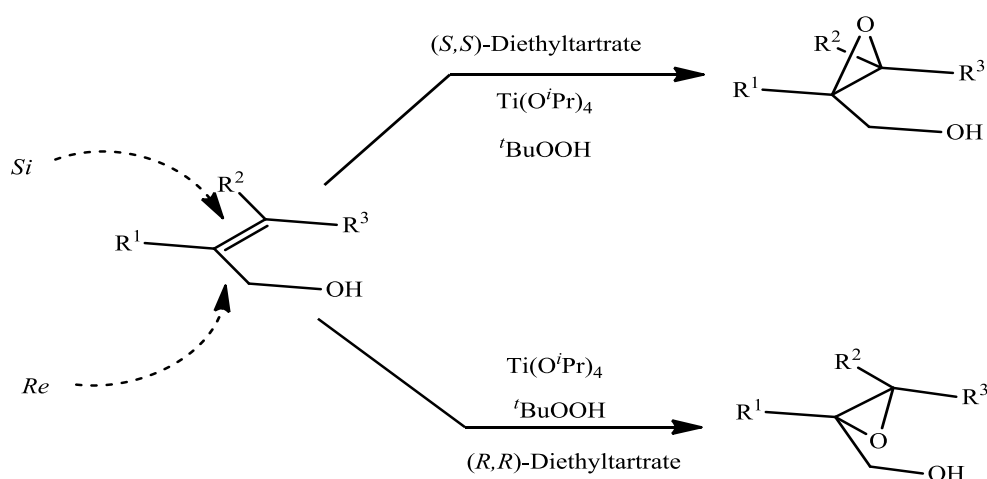


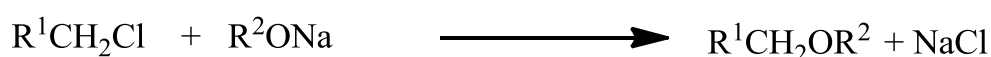
Figure 3: Sharpless asymmetric catalytic oxidation

In 2017, Prathap and co-workers have reported Nickel Boride mediated catalytic reduction of nitro compounds to amines in TEMPO oxidized nanocellulose in water at room temperature.²¹ Nanocellulose increase the turnover number and in this reaction nickel is only 0.25% is used and this reagent is much regio and chemoselective in excellent yield. A green procedure for oxidation of alcohols and reduction of

nitro compounds reported by Shokouhimehr *et.al.*²² In this conversion, the main reagent is hydroxyapatite supported Pd nanoparticles in water and this catalyst has great usability up to 6 cycles. Similarly, Coccia and co-workers have reported a green methodology for the synthesis of lignin stabilized Pt and Pd nanoparticles by using two natural polymers like lignin and fluvic acid.²³ Nanoparticles of both Pt and Pd are efficient for reduction of nitro compounds using sodium borohydride but Pt nanoparticles are effective to aerobic oxidation reactions.

There are various catalytic hydrogenation technique which are widely applied in industrial organic synthesis. Williamson ether synthesis first described in 1952 but this reaction requires strong basic condition. Similarly, catalytic alternative to the Williamson synthesis has been reported using aldehyde and alcohol in presence of catalytic hydrogen to give ether.²⁴⁻²⁵ This catalytic reaction avoids the side product NaCl and aldehydes are easily available and lesser toxic than alkyl halide. Moreover, Meerwein-Ponndorf-Verley (MPV) reduction reaction alternate are zeolites.²⁶⁻²⁷ In MPV reduction, aldehyde and ketone reduced to corresponding alcohols using isopropanol as reducing agent and Aluminum alkoxide as a catalyst. Aluminum alkoxide is used in stoichiometric amount but in case of Al- and Ti-beta zeolites are also able to do MPV reductions. Zeolites are present in solid form, can be separated by simple filtration and can be used up to 5 cycles.

Williamson ether synthesis



Catalytic alternative

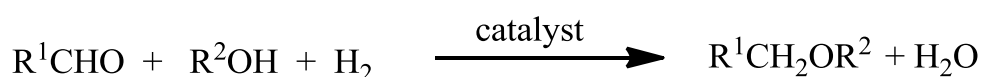
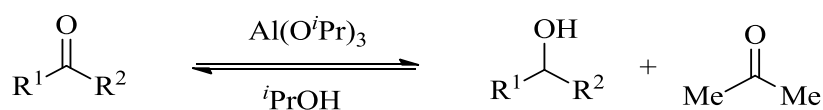
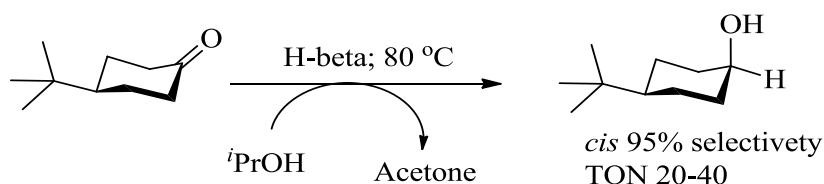
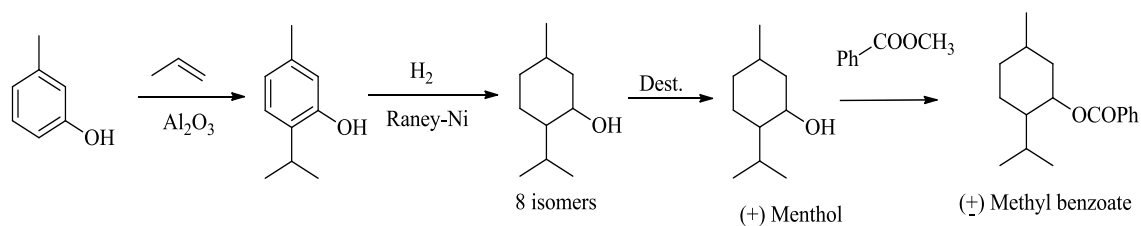


Figure 4: Williamson ether synthesis and its alternative synthesis

MPV reduction**Catalytic alternative****Figure 5:** MPV reduction and its alternative synthesis

Oxidizing agent like KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, CrO_2Cl_2 , PCC, AgNO_3 and ceric ammonium nitrate etc. are generally used oxidizing agents but all these oxidizing agents are used in stoichiometric amount and gave reduced metal as side product. In green alternate chemistry, many oxidizing agents such as molecular oxygen, H_2O_2 and NaOCl which are easily available and after oxidation gave the lesser toxic side product with higher selectivity. For example, there is 2 synthetic methodologies are present for the synthesis of menthol.²⁸⁻²⁹ In traditional method, there are total 5 steps including separation of different isomers and non-reusable metals & mineral acid reagents like Al_2O_3 , Raney-Ni were used but in second smaller methodology has only 3 steps and both the catalyst are reusable (Figure 6). All these reaction shows that the reusable catalyst increase the reaction efficiency as well as increase the atom efficiency of the reaction.

Traditional method



Alternative greener method

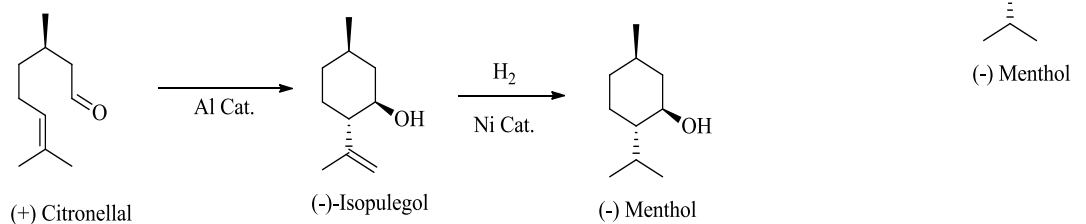


Figure 6: Traditional and greener method for the synthesis of Menthol

Electrochemical Synthesis: Chlorination bromination, nitration and alkylation are some well-known electrophilic aromatic substitution reactions. These reaction requires the various reagents for these reactions³⁰ and some common reagents for Chlorination bromination, nitration and alkylation are $\text{PhIO}+\text{AlX}_3$, Cl_2 , Br_2 , N -bromosuccinimide, HOBr , $\text{H}_2\text{SO}_4+\text{HNO}_3$, $\text{RX}+\text{AlX}_3$ but all these reagents partial hazardous to human body and aquatic life. Their isolation and reusability is negligible so atom efficiency of reaction decreases extensively. In recent times, electrochemical assisted gain tremendous interest due to its simplicity, low cost and it don't requires much oxidizing and reducing agents. The electrochemical methods work in a timely, sustainable and atom economic manner. The classical example of electrochemical method of synthesis is chloralkali process, wherein it requires only solution of sodium chloride to generate the chlorine gas and sodium hydroxide.³¹

Similarly in Hall-Heroult process, aluminum oxide provides elemental aluminum.³² Electrochemical based methodology provides mild reaction condition, chemoselectivity and great functional group tolerance. Oxidizing and reducing agents are not required in electrochemical assisted reactions because electric current act as oxidizing and reducing agents. Still the electrochemical reaction are not that common due to its complex setup and endless variables like electrode composition, electrolyte and cell type. Electrochemical cell shows various types of reactions like oxidation, reduction, deprotection, bromination, chlorination, nitration and alkylation etc.

In 2020, Niu and co-workers have reported the novel electrochemical assisted alkylation of quinoxalin-2(1*H*)-ones methodology in metal and additive free condition.³³ Traditional approach for alkylation requires the alkyl halide with AlCl₃ but AlCl₃ used in stoichiometric amount and not recoverable so it decrease the atom efficiency. In electrochemical reaction is catalyst free and hydroxyphthalimide ester act as alkylating reagent. Similarly, nitration requires the mineral acid like sulphuric acid and nitric acid which are non-recoverable and become hydrated during workup that leads to decrease in E-factor. Blum *et. al.* have demonstrated a novel electrochemical assisted nitration methodology using tetra-*n*-butyl ammonium nitrate as safer nitrating agent.³⁴ Graphite electrode converts nitrate ion to nitronium ion, which is mainly responsible for nitration and electricity act as green oxidant. Mild reaction condition, safer nitro source and regioselectively are merits of this greener methodology. Bromination of aryl/heteroaryl can be done in bromine in mineral acid or Lewis acid & *N*-bromosuccinimide but due to non-reusability of mineral acid and side product succinimide decrease the atom efficiency of reaction. Bromine is low melting liquid and at slightly higher temperature it get converted into brown fumes, which are hazardous for human health. Lv and co-workers invented novel electrochemical assisted bromination of aryl/heteroaryl using 2-bromoethan-1-ol as brominating agent.³⁵ Intramolecular reaction of 2-bromoethan-1-ol to give bromide ion, ethylene oxide and liberates hydrogen gas. In this methodology also electricity act as oxidizing

agent and scale up synthesis and functional group tolerance are merits of this methodology.

Sun and co-workers have achieved tremendous successful in the field of chlorination using electrochemical assisted reactions and NaCl act as chlorinating agent.³⁶ Formyloxylation and chlorination of alkene is carried out in one pot and DMF act as formylating agent. Electricity in this methodology also act as greener oxidizing agent and eliminates the use of harmful oxidizing agents. Leaded bronze emerged out as cathode material and strong reducing agent, which reduce the 1,1-dibromo cyclopropanes rings to cyclopropanes without affecting the cyclopropane ring.³⁷ Interestingly, this reaction also showed solvent effect as 1,1-dibromo cyclopropane converted into 1-bromo cyclopropane when acetonitrile solvent is used but complete reduced product is observed when DMF is used. In this methodology, leaded bronze act as reducing electrode and this reaction is very regioselective as it is applicable to very complex molecule like cyclosporine A.

Allylic oxidation is basically require selenium dioxide as a reagent but it is used in stoichiometric amount that decrease the atom efficiency and due to hazardous nature of selenium some alternate greener method need to be developed. In 2016, Horn and co-workers done the great job and developed a novel electrochemical assisted allylic oxidative methodology.³⁸ Wide functional group tolerance, sustainable and electricity as oxidizing agents are merits of this methodology.

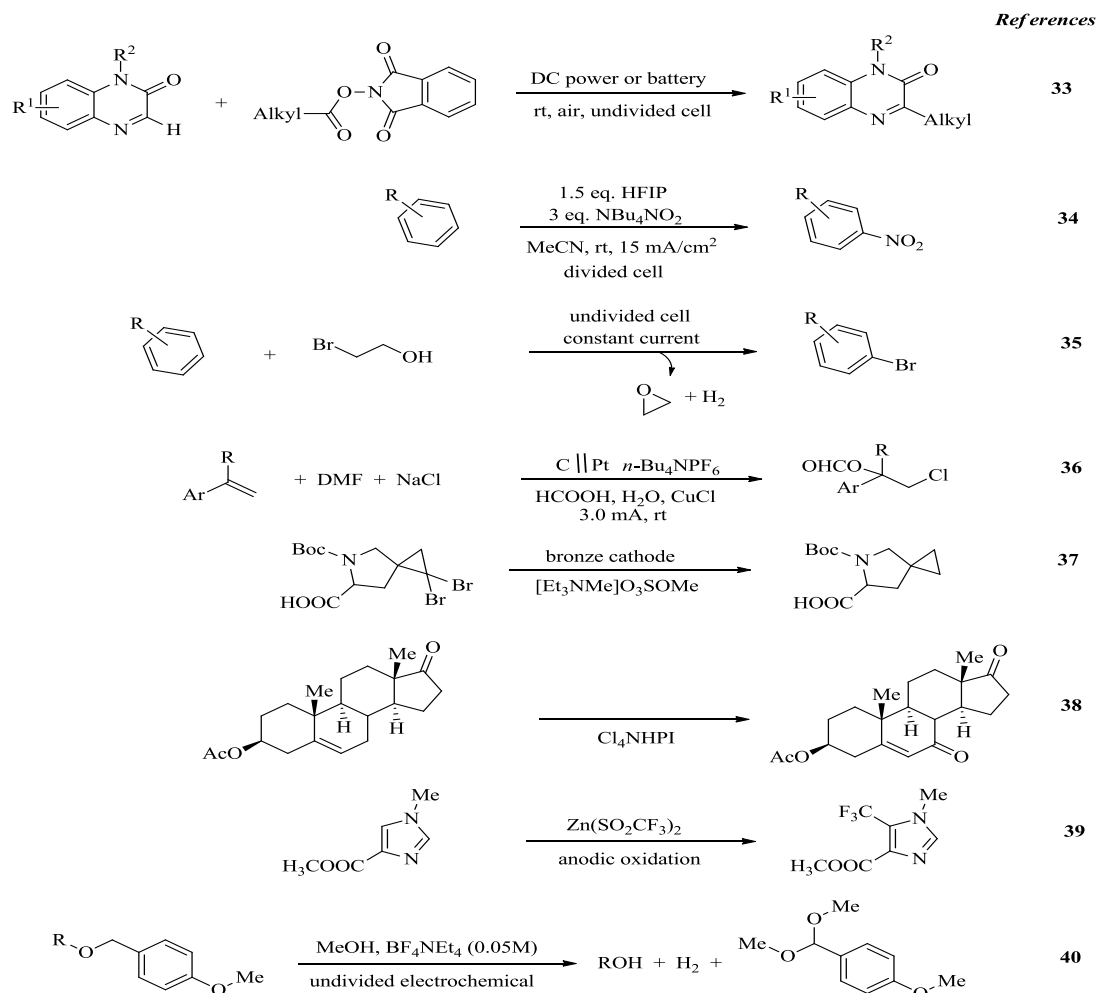


Figure 7: Electrochemical assisted some greener methodologies.

Fluoroalkylation of heteroarenes is most researched topic in recent times, generally some oxidant is used while doing fluoroalkylation to generate fluoroalkyl cation. O'Brien and co-workers have reported the oxidant free fluoroalkylation of heteroarenes under electrochemical oxidation.³⁹ In this methodology $Zn(SO_2CF_3)_2$ act as fluoroalkylating agent and has significant regioselectivity. Removal of sulfinate using electrochemical oxidation further increase the yield of product. Deprotection and protection are some essential steps in chemistry and they cannot be ignored. Deprotection of benzylic group is basically done by hydrogenation and metal hydrogenation reduce the reaction atom efficiency. Green and co-workers have reported a greener method for

deprotection of *p*-methoxybenzyl (PMB) ethers to give alcohol and *p*-methoxybenzaldehyde dimethyl acetal as side product.⁴⁰ Electrochemical cell removes the requirement of reducing agent and one reusable electrolyte (BF₄NEt₄) is used in this reaction.

Sonochemistry: Sonochemistry is the branch of chemistry that deals with the effect of ultrasonic sound on chemical reaction. Keeping in mind effect of electricity become electrochemistry similarly effect of ultrasound on chemical reaction become sonochemistry. In Ultrasound, we require only one liquid which generate cultivation to emit its power. Sonochemistry become new technique for energy conservation and waste minimization. Ultrasound working range is 20kHz to 500MHz, which is beyond the human ear hearing that lies between 16kHz to 20kHz. Sonicator generates and destruct the cavitation bubbles and at high power, bubbles collapse in compression cycle and that create the energy which have chemical and mechanical effects on chemicals. Bubbles collapse generates around 5000 °C temperature and 1000 atmospheric pressure.

In 2015, Fujita published a very interested paper based upon bromination of aromatic compounds using KBr as brominating agent and CCl₄/H₂O mixture act as oxidizing agent.⁴¹ When reaction of aromatic compound carried with KBr in presence of CCl₄/H₂O under otherwise identical condition but when similar reaction carried out on ultrasound the reaction gave brominating product (Figure 8).

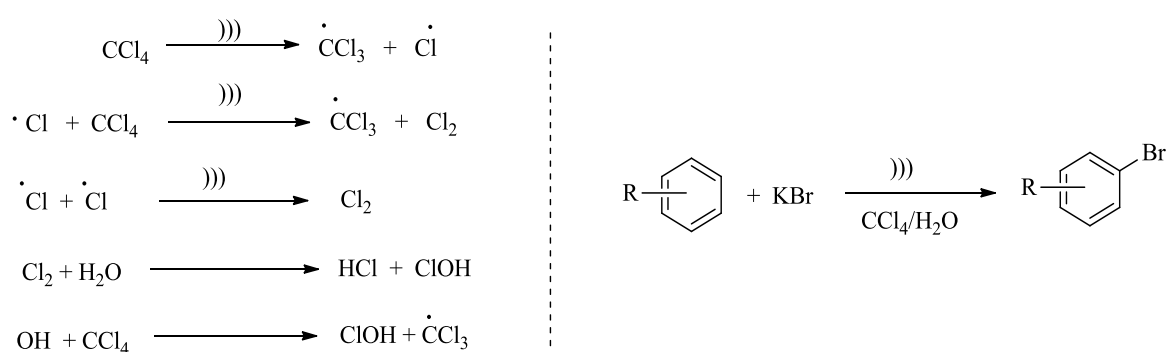


Figure 8: CCl₄/H₂O mediated bromination of aromatic compounds

Reactions in figure 8 suggest that water and carbon tetrachloride reacts with each other to give $\bullet\text{Cl}$, Cl_2 and HClO , which reacts with KBr to give bromine or bromine cation and that is responsible for bromination. This reaction removes all the traditional reaction in which oxidant or mineral acid is required for bromination and moved to much greener methodology. Similarly, when 4-nitrobenzyl bromide is treated with alkyl nitronate anion under traditional method gave the *p*-nitrobenzaldehyde while similar reaction under otherwise identical condition carried out in sonochemistry C-alkylated product is formed i.e. nucleophilic substitution reaction takes place because in sonochemical experiments reaction proceeds *via* radical mechanism (Figure 9).⁴² Similar effects are observed when styrene is treated with lead acetate under conventional heating for 1 hour gave the diacetate product in 5 percent yield only because reaction proceeds *via* ionic pathway but when similar compounds are treated under sonication gave mixture of product and in one case methylation of styrene also occurs because under sonication lead acetate dissociated to give methyl radical.⁴³ Sonication gave more enhanced yield product along with mixture of product that because of radical mechanism (Figure 9).

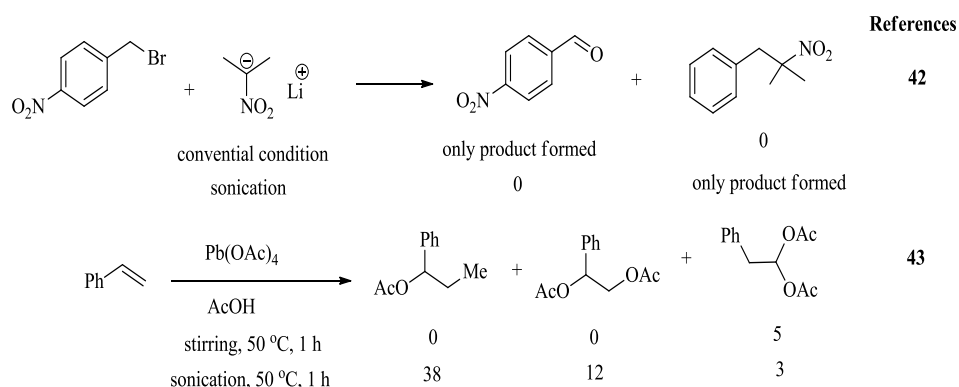


Figure 9: Conventional v/s sonication reactions

1, 3-dithianes and 1, 3-thiolanes of aromatic aldehyde/ ketones are deprotected by copper nitrate under sonicator irritation.⁴⁴ Frizzo and co-workers have studied the effect of solvent on product yield under sonicator irritation.⁴⁵ $[\text{BMIM}][\text{BF}_4]$ and water have highest dissipated ultrasonic power. No reaction is observed when hexane is

used as solvent. Nandurkar and co-workers have reported dilute nitric acid (8 wt%) mediated sonication assisted nitration of phenols.⁴⁶ The reaction shows considerable enhancement and selectivity under sonication. Reaction carried out under conventional condition gave only 30% yield after 48 hours but under sonication reaction get completed in 2 hours and gave 94% yield.

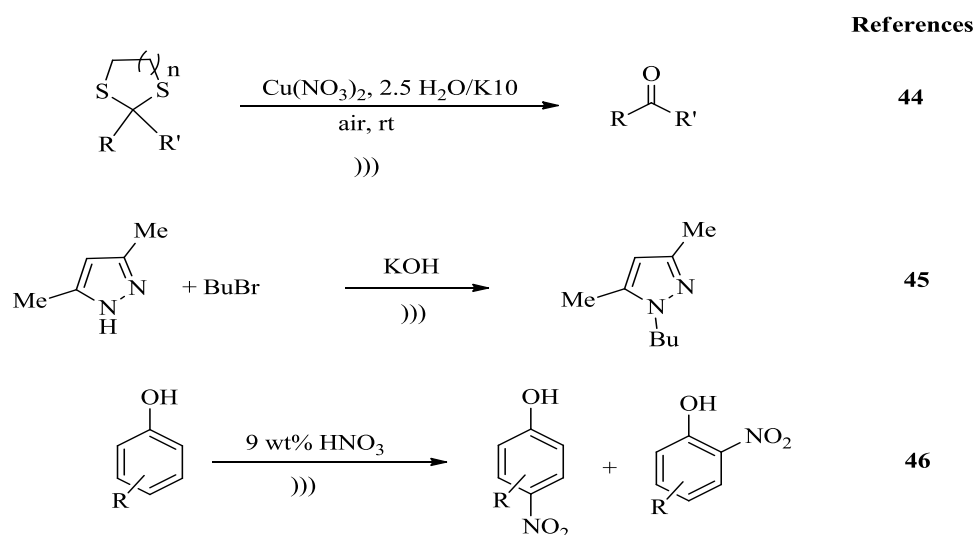


Figure 10: Deprotection and functionalization using sonochemistry

Mechanochemistry: Ball milling mechanochemistry emerged as a generally acceptable methodology of green chemistry because this methodology is solvent free, cleaner and faster than conventional methods. All these reaction enabled by mechanical force and all the reaction are undergoing rediscovery.⁴⁷ Mechanochemistry enables all those reactions that are difficult to do in solution and all the reaction were achieved by milling or grinding. Similarly, nitration of toluene can be carried out by treating with sodium nitrate and molybdenum trioxide under mechanochemical process.⁴⁸ The conventional methods require both nitric acid and sulphuric acid for the nitration and both are corrosive in nature and require specific handling of chemicals. The mechanical impact is observed in the reaction with the yields increasing with the amount of milling suggest that milling process helps in reaction acceleration also. Bera and co-workers have also extended the mechanochemical assisted C-N bond formation reaction

as well as the halogenation reactions.⁴⁹ In recent times, ball milling comes out as alternative chemical transformation because of its solvent free and milder reaction condition. *N*-Iodosuccinimide helps in cyclisation but *N*-bromosuccinimide and *N*-chlorosuccinimide helps in both cyclization as well as halogenation under mechanical condition.

Similarly in 2017, Troschke and co-workers have synthesized mechano- assisted framework by treating the cyanuric chloride with carbazole monomer to give alkylated porous covalent triazine frameworks.⁵⁰ This methodology elaborates the use of mechanochemistry in Friedel-Crafts alkylation and ball milling becomes the new methodology for the all known reactions and methodologies. Mechanochemical methodology also helps in multicomponent synthesis of various heterocyclic and carbocyclic compounds as this methodology increase the yield economy of the reaction due to its atom efficiency and economical friendly characteristics. Synthesis of oxazolones have reported by Fahmy *et. al.* treating glycine, benzoyl chloride, and aromatic aldehyde in presence of acetic anhydride and sodium acetate.⁵¹

Photochemistry: Light is the source of energy in photosynthesis of plants and that's why light or photons are always key area of research in mind of all chemists. Molecules absorb light due to which they have excited from ground level to excited level and excitation from ground level to excited level may leads to the product formation. These days photochemical reactions are in interest because these reactions are carried out in visible light or sun light (renewable) makes it main topic of green chemistry. There are many reactions which can be carried out but we will discuss only general idea of photochemical assisted reaction in nitration, halogenation, alkylation and sulfonylation. In 2017, McCallum and co-workers reported the photochemical assisted alkylation and reduction of heteroarenes.⁵² Alkylation generally requires the Lewis acid but in presence of HCl under UVA-LED light irradiation gave the alkylated product. In this methodology, alcohol or ether act as alkylating reagent but when

same reaction is carried out in presence of *i*-propyl alcohol reduces the heteroaryl ring under otherwise identical condition. Sandmeyer reaction is mediated by copper halides and gave haloarene from aryldiazonium salts. Green chemistry says that removing the metal ion from reaction is considered under green chemistry. Sivendran *et. al.* have reported alternate method of Sandmeyer reaction and synthesized the photochemical assisted haloarenes from the aryldiazonium salts in presence of trihalide salts.⁵³ Recently, Liu and co-workers have displayed the catalyst free and additive free photochemical assisted sulfonylation of phenothiazines using arylsulfonyl chloride as sulfonylating reagent. In this methodology, phenothiazines act as both reactant and a photosensitizer. Generally sulfonylation requires the lewis acid catalysis but under photochemical assisted reaction, no reagent is required and all these examples of alkylation, reduction, halogenation and sulfonylation suggest that photochemical chemistry is future of green chemistry and eliminates the reagents for some extent.

Harsh and co-workers have elaborated the chlorophyll assisted synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones under concentrated solar energy in solvent free condition.⁵⁴ The reaction between aldehyde, urea and ethyl acetoacetate in presence of chlorophyll under concentrated solar radiation gave the 3,4-dihydropyrimidin-2(1*H*)-ones in excellent yield. The reaction gave only 8% of desired product when the reaction was carried out without chlorophyll, which suggest that in this reaction chlorophyll act as photocatalyst or photosensitizer. The reaction gave inferior yield of desired product when reaction was optimized in blue light and sun light. When the TEMPO is used in reaction mixture under otherwise identical condition gave the trace amount of product suggest that the reaction proceeds *via* radical mechanism. Chlorophyll and haemoglobin are proven photosensitizer because its absorption energy lies in visible region and effective in solar radiation (400-700 nm).

II. CONCLUSION

In this chapter we have discussed the all the modern green chemistry reactions and methodologies which reduces the side product, increase the yield and atom economy. All the green chemistry methodologies are discussed in this chapter like solid acid catalyzed reactions, greener oxidation and reduction reactions, electrochemical reactions, sonochemical, photochemical and mechanochemical reactions. Easy isolation of products, safer chemicals, greener solvents and renewable energy source are some merits of all these methodologies

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