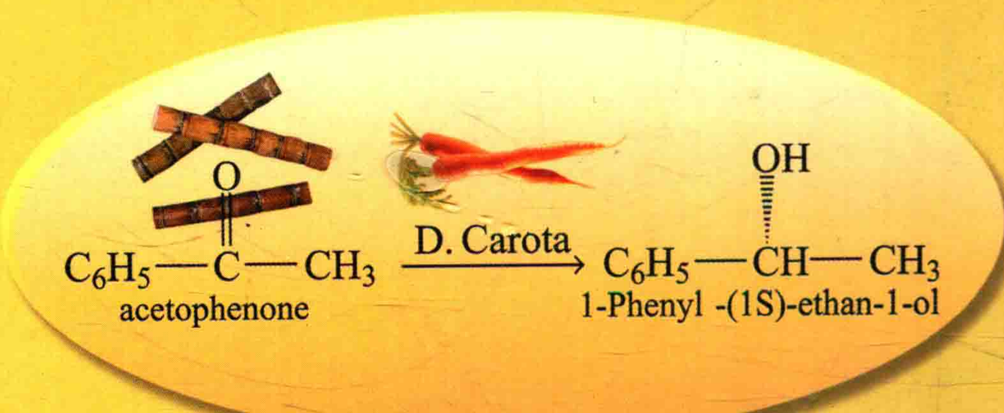
GREEN CHEMISTRY

Environmentally Benign Reaction



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Environmentally Benign Reactions

Preface

Green chemistry is basically environmentally benign chemical synthesis and is helpful to reduce environment pollution. A large number of organic reaction were earlier carried out under anhydrous conditions and using volatile organic solvents like benzene, which cause environmental problems and are also potential carcinogenic. Also the bye products are difficult to dispose of.

With the advancements of knowledge and new developments, it is now possible to carry out large number of reactions in aqueous phase, using phase transfer catalysts, using sonication and microwave technologies. Some reactions have also be performed enzymatically and photochemically. It is now possible to carry out a number of reactions using the versatile liquids and also in solid state.

The book is divided into three chapters. Introduction to Green Chemistry is described in Chapter 1. The second chapter deals with those reactions which are now performed under the so called green conditions. Such reactions are now referred to as Green Reactions.. Finally in chapter 3 are described a number of preparations in aqueous phase, using phase transfer catalysis using sonication and microwave technologies. Also some preparation carried out enzymatically and photochemically. It is now possible to perform by using ionic liquids as solvents are also described.

The author expresses his sincere thanks to Dr. Pooja Bhagat, Dr. Madhu Chopra for all the help they have rendered.

Grateful thanks are due to Prof. Sukh Dev FNA, INSA Professor, New Delhi, Prof. J. M. Khurana, Department of Chemistry and Dr. R. K. Suri, Additional Director, Ministry of Forests, Government of India.

Finally I take the opportunity to thank Prof. Ramesh Chandra, Director, Dr. B. R. Ambedkar Centre for Biomedical Research University of Delhi, Delhi for all the help rendered.

V. K. Ahluwalia

Foreword

I feel happy to congratulate Prof. V. K. Ahluwalia on his writing a book on "Green Chemistry - Environmentally Benign Reactions". The book is replete with basic principles of Green Chemistry and requisite details that are necessary to obtain a desirable organic reactions (which earlier needed anhydrous conditions and used volatile organic solvents) under green condition. It is hoped that this development will go a long way in reducing not only environmental pollution but also effecting atom economy.

The book has been very well written and presented in a lucid manner. The book is so comprehensive that it can serve as a practical guide to the researchers (including M.Sc., M.Phil. and Ph.D) in various Industries, Universities and College Laboratories.

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Green Chemistry

INTRODUCTION

Green chemistry is defined as environmentally benign chemical synthesis. It focusses on a process (whether carried out in industry or chemical laboratory) that reduce the use and generation of hazardous substances or byproducts. Strict laws have been passed by various governments particularly in advanced countries like USA to strictly follow the procedures for various synthesis so as to reduce or eliminate the products (or by products) that are responsible for the pollution of the environment. The chemists all over the globe are motivated not only for the environmentally benign synthesis of new products but also to develop green synthesis for existing chemicals. This has been possible by the replacement of the organic solvents, which are hazardous by water or eliminate the use of solvent altogether.

There is absolutely no doubt that green chemistry has brought about medical revolution (e.g., synthesis of drugs etc.). The world's food supply has increased many fold due to the discovery of hybrid varieties, improved methods of farming, better seeds and use of agro chemicals like fertilizers, insecticides and herbicides etc. Also the quality of life has improved due to the discovery of dyes, plastics, cosmetics and other materials. All these developments increased the average life expectancy from 47 years in 1900 to 75 years in 1990's. However, the ill effects of all the development became pronounced. The most important effect is the release of harzardous by products of chemical industries and the release of agro chemicals in the atmosphere, land and water bodies; all these are responsible for polluting the environment including atmosphere, land and water bodies. Due to all these green chemistry assumed special importance.

1.1 THE NEED OF GREEN CHEMISTRY

It has already been stated that various scientific developments in the 20th century brought about various benefits to the mankind, but all this was responsible for a number of environmental problems at the local and global levels. It is, of course, important to formulate guidelines and pass strict rules for the practicising chemists. But the most important is to bring about changes at the grass root level. And this can be achieved by bringing about necessary changes in the chemistry curriculum in the colleges and the universities and also in the secondary schools. A concerted and pervasive effort is needed to reach the widest audience. Bringing green chemistry to the class room and the laboratory will have the desired effect in educating the students at various levels about green chemistry.

1.2 PRINCIPLES OF GREEN CHEMISTRY

Green chemistry deals with environmentally benign chemical synthesis with a view to devise pathways for the prevention of pollution. According to Paul T. Anastas,[1] the following twelve basic principles of green chemistry have been formulated.

1. **It is better to prevent waste than to treat or clean up waste after it is formed.**
   It is best to carry out a synthesis by following a pathway so that formation of waste (by products) is minimum or absent. It must be kept in mind that in most of the cases, the cost involved in the treatment and disposal of waste adds to the overall cost of production. The unreacted starting materials (which may or may not be hazardous) form part of the waste. The basic principle 'prevention is better than cure' should be followed. The waste if discharged in the atmosphere, sea or land not only causes pollution but also requires expenditure for cleaning up.
2. **Synthetic materials should be designed to maximize the incorporation of all materials used in the process into the final product.**
   It has so far been believed that if the yield in a particular reaction is about 90%, it is considered to be good. The percentage yield is calculated by

   $$\%\ \text{yield} = \frac{\text{Actual yield of the product}}{\text{Theoretical yield of the product}} \times 100$$

   The above calculation implies that if one mole of a starting material produces one mole of the product, the yield is 100%. However, such a synthesis may generate significant amount of waste or by products which is not visible in the above calculation. Such a synthesis, even though is 100% (by above calculation) is not considered to be a green synthesis. For example, reactions like Grignard reactions and Wittig reaction may proceed with 100% yield but they do not take into account the large amount of by products obtained.

   A reaction or a synthesis is considered to be green if there is maximum incorporation of the starting materials or reagents in the final product. One should take into account the percentage atom utilization, which is determined by the following equation

   $$\%\ \text{atom utilization} = \frac{\text{MW of desired product}}{\text{MW of desired product} + \text{MW of waste products}} \times 100$$

   This concept of atom economy was developed by B.M. Trost[2] in a consideration of how much of the reactants end up in the final product.

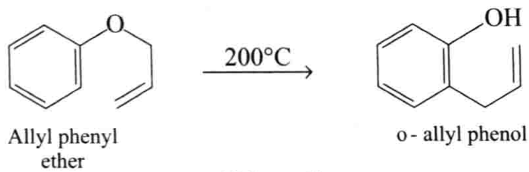
The same concept was also determined by R.A. Sheldon[3] as given below.

$$\%\text{ atom economy} = \frac{\text{FW of atoms utilized}}{\text{FW of the reactants used in the reaction}} \times 100$$

The most common reaction we generally come across in organic synthesis are rearrangement, addition, substitution and elimination reactions. Let us find out which of the above reactions is more atom economical.

(a) Rearrangement Reactions

These reactions involve rearrangement of atoms that make up a molecule. For example, allyl phenyl ether on heating at 200°C gives o-allyl phenol (Scheme-1).



(Scheme-1)

The rearrangement reaction (in fact all rearrangement reactions) is 100% atom economical reaction, since all the reactants are incorporated into the product.

(b) Addition Reactions

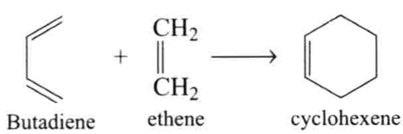
Consider the bromination of propene (Scheme-2).

$$\underset{\text{Propene}}{H_3C\,CH{=}CH_2} + Br_2 \xrightarrow{CCl_4} \underset{\text{1,2-dibromopropane}}{H_3C\,CH\,Br\,CH_2Br}$$

(Scheme-2)

Here also all elements of the reactants (propene and bromine) are incorporated into the final product (1,2-dibromopropane). So this reaction is also 100% atom economical reaction.

In a similar way cycloaddition reaction of butadiene and ethene (Scheme-3) and addition of hydrogen to an olefin (Scheme-4) is 100% atom economical reaction.



(Scheme-3)

$$\underset{\text{Propene}}{H_3C{-}CH{=}CH_2} + H_2 \xrightarrow{Ni} \underset{\text{Propane}}{H_3C{-}CH_2{-}CH_3}$$

(Scheme-4)

(c) Substitution Reactions

In substitution reactions, one atom (or group of atoms) is replaced by another atom (or group of atoms). The atom or group that is replaced is not utilised in the final product. So the substitution reactions are less atom economical than rearrangement or addition reactions.

Let us consider the reaction of ethyl propionate with methyl amine (Scheme-5).

(Scheme-5)

In the above reaction, the leaving group (OC_2H_5) is not incorporated in the formed amide and also, one hydrogen atom of the amine is not utilized. The remaining atoms of the reactants are incorporated into the final product.

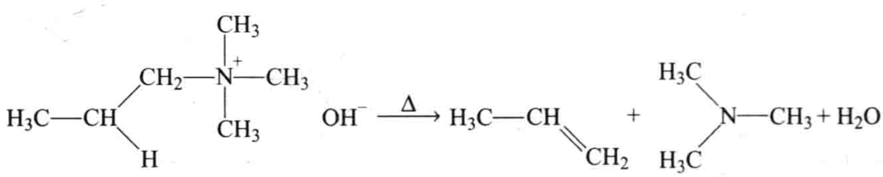
The total of atomic weights of the atoms in reactants that are utilized is 87.106 g/mole, while the total molecular weight including the reagent used is 133.189 g/mole. Thus a molecular weight of 46.069 g/mole remains unutilized in the reaction.

	Reactants		*Utilized*		*Unutilized*	
	Formula	*FW*	*Formula*	*FW*	*Formula*	*FW*
	$C_5H_{10}O_2$	102.132	C_3H_5O	57.057	C_2H_5O	45.061
	CH_5N	31.057	CH_4N	30.049	H	1.008
Total	$C_6H_{15}NO_2$	133.189	C_4H_9NO	87.106	C_2H_5OH	46.069

Therefore, the atom economy (%) = $\frac{87{\cdot}106}{133{\cdot}189} \times 100 = 65.40\%$

(d) Elimination Reactions

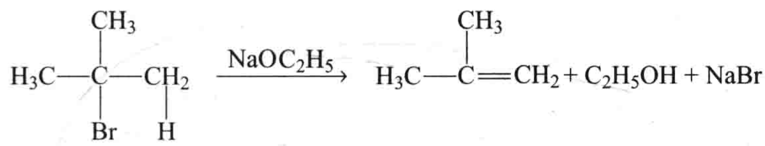
In an elimination reaction, two atoms or groups of atoms are lost from the reactant to form a π bond. Consider the following Hofmann elimination reaction (Scheme-6).



(Scheme-6)

The above elimination reaction is not very atom economical. The percentage atom economy is 35.30% and is the least atom economical of all the above reactions.

Consider another elimination reaction involving dehydrohalogenation of 2-bromo-2-methylpropane with base to give 2-methylpropene (Scheme-7).



2-Bromo-2-methylpropane 2-Methyl propene

(Scheme-7)

The above dehydrohalogenation reaction (an elimination reaction) is also not very atom economical. The percentage atom economy is 27% which is even less than the Hofmann elimination reaction.

3. **Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.**
   One of the most important principle of green chemistry is to prevent or at least minimize the formation of hazardous products which may be toxic and or environmentally harmful. In case hazardous products are formed, their effects on the workers must be minimized by the use of protective clothing, respirator etc. This, of course, will add to the cost of production. At times, it is found that the controls may fail and there may be more risk involved. Green chemistry, in fact, offers a scientific option to deal with such situations.

4. **Chemical products should be designed to preserve efficacy of function while reducing toxicity.**
   It is extremely important that the chemicals synthesised or developed (e.g., dyes, paints, cosmetics, pharmaceuticals etc.) should be safe to use. A typical example of an unsafe drug is thalidomide (introduced in 1961) for reducing the effects of nausea and vomitting during pregnancy (morning sickness). The children born to women taking thalidomide suffered birth defects. Subsequently, the use of thalidomide was banned, the drug withdrawn and strict regulations passed for testing all new drugs.
   With the advancement of technology, the designing and production of safer chemicals has become possible. In fact, it is possible to manipulate the molecular structure to achieve this goal.

5. **The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.**
   A number of solvents like methylene chloride, chloroform, perchloroethylene, carbon tetrachloride, benzene and other aromatic hydrocarbons have been used (in a large number of reactions) due to their excellent solvent properties. However, the halogenated solvents (mentioned above) have been identified as suspected human carcinogens. Also, benzene and other aromatic hydrocarbons are believed to promote cancer in humans and other animals.