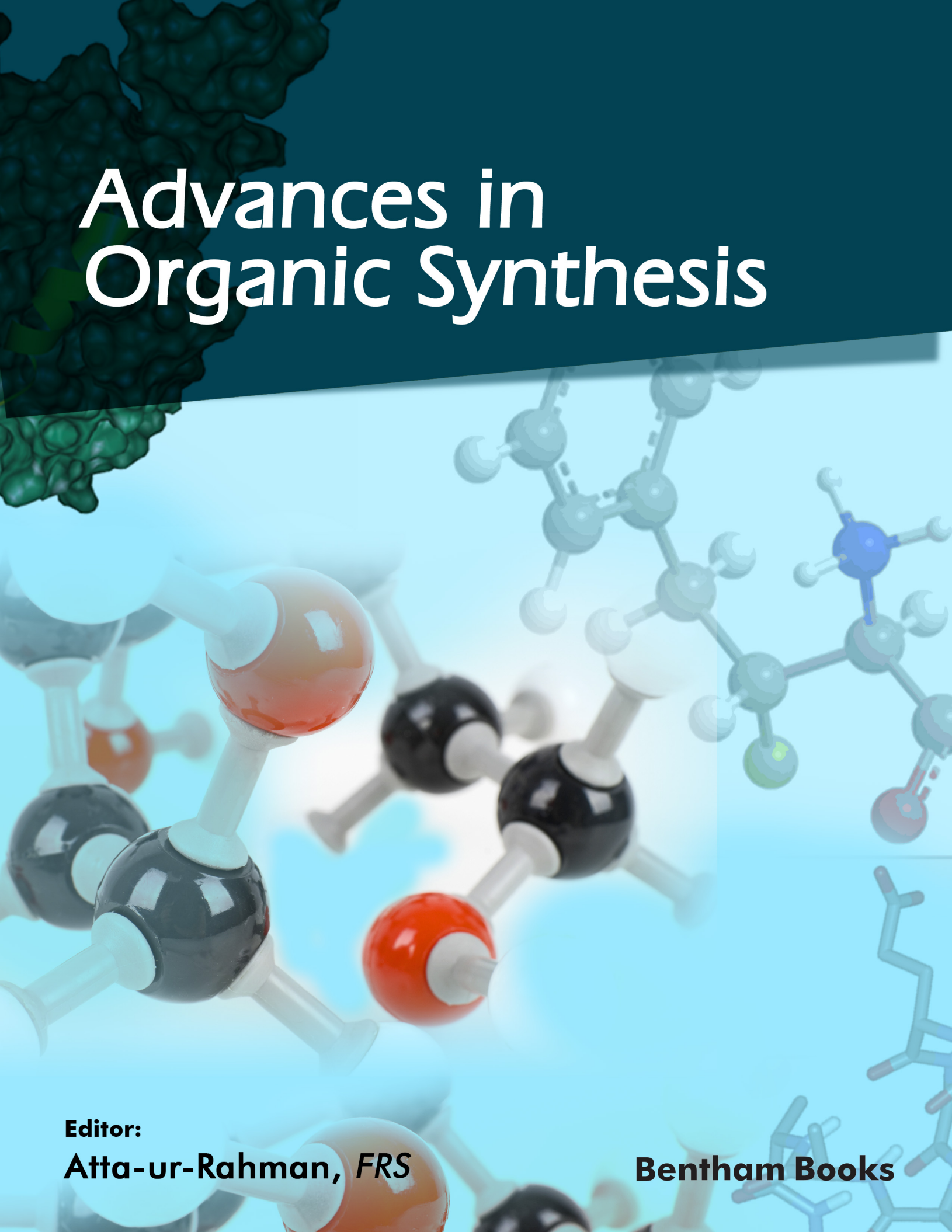
Advances in Organic Synthesis



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PREFACE

The 16th volume of ***Advances in Organic Synthesis*** presents recent exciting developments in synthetic organic chemistry. The chapters are written by eminent researchers in the field. The topics include advances in copper-catalyzed heterocyclic syntheses, modern green chemistry methods, review on electroluminescence polymers, synthesis of xanthene, evolution of polymer chemistry, and lastly, an overview on oxidizing and reducing agents in total synthesis.

This volume should prove to be a valuable resource for organic chemists, pharmaceutical scientists and postgraduate students seeking updated and critically important information on recent important developments in synthetic organic chemistry. I hope that the readers will find these reviews valuable and thought-provoking, and that they trigger further research in the quest for new developments in the field.

I am thankful to the efficient team of Bentham Science Publishers for the timely efforts, especially the editorial personnel Mr. Mahmood Alam (Editorial Director), Mr. Obaid Sadiq (Incharge eBooks Department), and Ms. Asma Ahmed (Manager Publications).

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CHAPTER 1

Recent Advances in Copper-catalyzed Heterocyclic Syntheses

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Abstract: Heterocycles have gained significant attention from the research community due to their prevalence in numerous natural products and their applications as pharmaceuticals, agrochemicals, and new materials. The application of transition metal catalysts in the synthesis of heterocyclic compounds is an indispensable tool in the field of organic synthesis and has acquired notable recognition in scientific society all over the world. The popularity of copper-based catalysts is attributed to their cost-effectiveness, easy accessibility, and environmentally benign nature. In addition to this, the ability of copper catalysts to coordinate with heteroatoms and to activate unsaturated systems has resulted in the growing interest of synthetic and medicinal chemists in this field. Copper-based catalysts have shown their application in various cross-coupling reactions, C–H functionalization, radical alkylations, conjugate additions, and trifluoromethylation. Furthermore, they have also exhibited tremendous scope in heterocyclic syntheses, which include many important reactions, such as azide-alkyne click reaction (a type of 1,3-dipolar cycloaddition), nitrone-olefin cycloaddition (Kinugasa reaction), multi-component reactions, and other similar strategies which result in the construction of 4-8 membered heterocyclic adducts of biological and industrial relevance. The copper-catalyzed heterocyclic syntheses have many advantages, such as easily accessible substrates, good atom economy, high functional group tolerance, excellent yields, and remarkable selectivities. In addition to this, the targetted heterocycles exhibited diverse biological activities *viz.* antibacterial, antifungal, anticancer, antitubercular, anti-HIV, anti-inflammatory, analgesics, and antiviral activities. The main aim of this chapter is to summarize the advances made in copper-catalyzed synthesis of heterocyclic compounds in the last ten years.

Keywords: Asymmetric, Azide-alkyne cycloaddition, Click reaction, Copper-catalyzed, Cyclization, Cycloaddition, Diastereoselective, Enantioselective, Heterocycles, Heterocyclic syntheses, Kinugasa reaction, Multicomponent.

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INTRODUCTION

Heterocyclic compounds represent an important and broad division of organic chemistry. These compounds are widely distributed in nature. A large number of naturally occurring compounds, such as amino acids, vitamins, nucleic acids, antibiotics, and related compounds, possess heterocyclic core, which can attribute to their unique structural characteristics [1]. Heterocyclic compounds have played an essential role in the metabolic activity of all living cells. Furthermore, heterocycles have also found numerous applications in various industries, *viz.* pharmaceutical, agrochemical, *etc* [2, 3]. The use of heterocycles as modifiers and additives in reprography, cosmetics, plastics, and information storage materials has significantly enhanced the scope of this field. In addition to medicinal applications, heterocyclic molecules have exhibited other useful applications, such as fungicides, herbicides, anticorrosive agents, photostabilizers, dyestuff, copolymers, photographic developers, sensitizers, whiteners, and flavouring agents [4]. The heterocyclic compounds have attracted considerable interest from the scientific community due to their valuable and versatile applications (Fig. **1**).

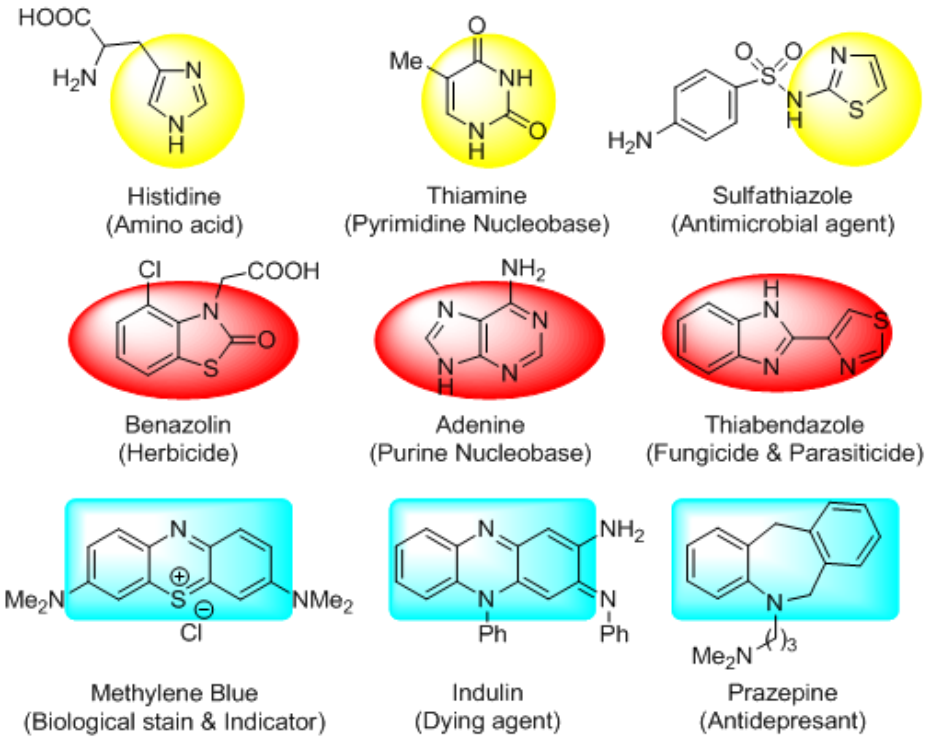

Fig. (1). Biologically important heterocyclic compounds.

Apart from natural resources, synthetic chemistry has also provided access to a wide range of heterocyclic compounds. It has been found that most of the new synthetic drugs contain heterocyclic core in their structure. Synthetic heterocyclic compounds are widely known for their therapeutic activity, such as antibacterial, antifungal, anti-HIV, antitubercular, antimalarial, anticancer, anti-inflammatory antidepressant, and insecticidal [4].

The present chapter is divided into different sections, *viz.* Classification, General synthesis of heterocycles and Chemistry & applications of copper. The last section, *i.e.,* Recent trends in copper-catalyzed heterocyclic syntheses, deals with the literature reports of the past ten years which have been selected for demonstrating the advancement made in this field.

CLASSIFICATION

Organic Compounds

Organic compounds are broadly classified into two categories, namely acyclic compounds and cyclic compounds (Fig. **2**). Acyclic compounds refer to those compounds having long chains of the carbon skeleton. These are also known as open-chain compounds. These compounds are further categorized into straight-chain compounds and branched-chain compounds (Fig. **2**). On the other hand, cyclic compounds are those compounds that possess ring structures. The cyclic compounds are further classified into homocyclic compounds and heterocyclic compounds (Fig. **2**). Homocyclic compounds are those in which cyclic ring is made up of only one type of atom, *i.e.,* Carbon, whereas heterocyclic compounds are those in which one/more heteroatoms are present in the ring system in addition to carbon.

Heterocyclic Compounds

Generally, heterocyclic compounds are categorized as small-sized heterocycles (three and four-membered rings), medium-sized heterocycles (five and six-membered rings), and large-sized heterocycles (Seven or higher membered rings). Small-sized heterocycles are highly strained molecules, therefore, they are highly reactive in nature. Furthermore, five- and six-membered heterocyclic rings are quite stable, hence, they are present in a majority of biologically and industrially relevant heterocycles. These heterocycles are present either as an isolated ring or fused heterocyclic system. The seven and higher membered heterocycles are not very much investigated since they are less readily formed. However, the application of these compounds in medicinal chemistry and material sciences continues to thrive more interest of the researchers in this field [5, 6].

CHAPTER 2

Application of Modern Green Chemistry Methods in the Synthesis of Quinolines, Quinazolines and Quinazolinones

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Abstract: In the last few decades, there is a constant demand for novel bioactive compounds in all areas of pharmacy and medicine, thus increasing the demands for their design and synthesis. Quinolines, quinazolines and quinazolinones, highly bioactive heterocyclic compounds with a nitrogen core, have been employed in many important drugs nowadays. Their synthesis often includes an enormous amounts of different hazardous organic solvents, catalysts, as well as energy consumption. In the last two decades, there is a growing interest in the application of different green chemistry methods in different research areas, including synthesis. This chapter describes their application in the synthesis of the above mentioned compounds. Microwave-assisted, ultrasound-assisted, mechanochemical synthesis in the combination with solvent-free synthesis and synthesis in deep eutectic solvents (DESs) and ionic liquids (ILs) of quinolines, quinazolines and quinazolinones is described. All mentioned green chemistry methods are gaining promising environmental and economic benefits and are being a subject of many research these days.

Keywords: Deep eutectic solvents, Mechanochemical synthesis, Microwave-assisted synthesis, Quinazoline, Quinazolinone, Quinoline, Solvent-free synthesis, Ultrasound-assisted synthesis.

INTRODUCTION

Nowadays, the principles of Green Chemistry have been accepted and applied by many scientists, who are becoming aware of the risks and adverse effects caused by the use of common organic solvents, both on their health and the environment.

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In order to reduce the utilization of such harmful chemicals, new green approaches were developed. Such green methods are widely used in many chemical and industrial processes, as well as in the preparation of various heterocycles.

The use of microwave irradiation as a heating source can significantly reduce reaction time from hours to minutes, as well as energy consumption required for chemical transformations. This phenomenon is attained by irradiation of polar molecules due to the absorption of microwaves converted into the heat [1]. Microwave-assisted synthesis has found a place in many chemical transformations such as condensation, rearrangement, redox reaction and protection of different functional groups. All the reactions in polar solvents induced by microwaves lead to better conversion of reactants, pure products and minimizing the use of organic solvents. Another efficient green method, used to accelerate organic reactions, is ultrasound-assisted synthesis. A large number of experiments can be carried out in excellent conversions, milder conditions and shorter reaction times. The ultrasonic waves with small amplitudes cause cavitation of the bubbles, which then enhance the efficiency of the overall process [2]. Mechanochemical synthesis usually involves solid-state reactions with the absorption of mechanical energy. Grinding, milling and shearing are three types of applied mechanochemical processes in many fields. The desired products can be prepared with no or minimal side reactions, leading to better yields and conversions. Mechanochemical synthesis is often combined with solvent-free synthesis. The benefits of solvent-free synthesis are the absence of hazardous solvents, the reduction of byproducts and less consumption of energy and solvents [3, 4]. To enhance the green character of the reactions, many researchers have been replacing conventional organic solvents with less adverse ones. Ionic liquids (ILs) and deep eutectic solvents (DESs) have been usually applied in this manner. ILs are composed of ions, usually an organic cation and polyatomic inorganic anion, and most of them exist as liquids at ambient temperature. Moreover, asymmetrical cation is preferable for their preparation due to unique properties. Negligible vapor pressure, non-volatility, low viscosity, thermal stability and high dissolving capacity are only some of their advantages, compared to the use of conventional organic solvents [5]. They are also referred to as a "*designer solvents*", since the combination of different ions produces desirable solvent properties. Therefore, there is a huge application of ILs in many research areas. For example, they are used in the synthesis often both as a solvent and catalyst [6, 7], biocatalyst [8], in modification of polymers [9], as electrothermal sensors [10], *etc.* On the other side, the greenness of ILs is questionable, since some ions used for their preparation are highly hazardous, such as imidazolium, piperidinium, pyridinium cations. Their toxicity was examined in some relevant papers on bacteria [11], human cells [12] and plant growth [13]. It has been observed that the introduction of an ester group into alkyl chains improves the ecotoxicity of ILs. However, due to their reusability,

recyclability, non-detectable vapour pressure and improvements in the conversion of reactions over conventional solvents, ILs are very useful in green synthetic chemistry. The second type of solvents, DESs, was reported in 2003. Deep eutectic solvents have numerous advantages over conventional organic ones. They are usually comprised of a hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA), which form a eutectic mixture through the formation of the net of hydrogen bonding. Their impressive physical and chemical properties arise from this network of hydrogen bonds, showing a low vapor pressure, biodegradability, non-toxicity and low cost. These are the reasons they have been increasingly used in organic synthesis, both as solvents and catalysts [14, 15]. This book chapter provides a concise overview on the practical aspects of modern green chemistry methods in the synthesis of quinoline, quinazoline and quinazolinone derivatives.

QUINOLINES

Quinoline, 1-azanaphtalene or benzo[*b*]pyridine, is a fused heterocyclic compound with weak basic properties (Fig. **1**). It was discovered as a colorless liquid in 1834 by Friedlieb Rouge. Quinoline and its derivatives show considerable attention in medicinal and pharmaceutical chemistry as great pharmacophores [16].

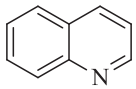

Fig. (1). Structure of quinoline [8].

Microwave-assisted Synthesis

In their attempt to synthesize biologically active quinolone/imidazole hybrids, Desai *et al*. compared conventional and microwave-assisted synthesis. A Perkin condensation was performed, starting from 2-chloroquinoline-3-carbaldehyde, hippuric acid, acetic anhydride and anhydrous sodium acetate. This reaction was completed in 3 minutes, when microwaves were used. The obtained 4-((--chloroquinolin-3-yl)methylene)-2-phenyloxazol-5(4*H*)-one was then reacted with *N*-aminoarylcarboxamides, with 2-3 drops of pyridine in DMF to yield **1** (Scheme **1**). The overall reaction time for the synthesis of the final products, when performed conventionally, was 10-13 h. When microwaves were applied, the same reaction was finished within minutes. The excess of pyridine was neutralized with concentrated hydrochloric acid, the crude product was filtered, washed with water and recrystallized from ethanol. Not only the time was the advantage of this method, but the final yield as well. Improvements in yield up to 78% are observed with microwave heating concerning conventional heating [17].

CHAPTER 3

Electroluminescence Polymers-a Review on Synthesis by Organic Compounds

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Abstract: In the past, no one believed that polymers could prove to be effective Light-Emitting Diodes (LEDs). Very few research groups understood that the polymer light displayed semiconducting and electrical properties. However, it has been observed that the polymer LEDs can be used in many larger display arrays as they show mechanical flexibility and can be processed easily. The different polymers can be synthesised using reactive organic compounds, called monomers, which consist of a minimum of two functional groups. In this review, the researchers described a synthesis route for many organic monomers which can be converted to form LEDs. They have detailed the development of the polymers right from their inception. Furthermore, this review described the major mechanism related to light emission and all relevant problems associated with colour tuning. After investigating the polymer LEDs, the researchers noted that various light colours could be emitted efficiently, with uniformity and brightness. The colour of this emitted light was dependent on the band gap of π-π transition, which seem to be the function of the structure of the polymer. Hence, any modification could affect the band gap and the colour that was emitted. For developing efficient PLEDs, many factors were considered, like stable radiative transitions for the singlet excitons, balance of electrons and holes and light extraction. It was seen that the fabrication of phosphorescence emitters using the triplet-triplet energy transfer approach was an effective strategy for obtaining a high-efficiency luminescence. This review also highlighted the main routes for the fabrication and processing of the devices.

Keywords: Colour tuning, Conjugated polymers, LED device, Organic LED, Polymeric LEDs.

INTRODUCTION

Luminescence is described as the emission of visible, ultraviolet or infrared light photons by an electronically-excited species. The term ‘luminescence’ is derived from Latin (lumen means light) by Eilhardt Wiedemann in 1888, who was a science historian and physicist.

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He defined 'luminescent' as a light phenomenon that is not based on the increase in temperature, unlike incandescence. Rather, luminescence is a cold light phenomenon, while incandescence is a hot light phenomenon. There are different types of luminescent compounds as described below:

1- Organic compounds - Include aromatic hydrocarbons (like anthracene, naphthalene, pyrene, perylene, *etc.*), rhodamines, diphenyl polyenes, fluorescein, oxazines, coumarins, polyenes, amino acids (such as tyrosine, tryptophan and phenylalanine).
2- Inorganic compounds - Include lanthanide ions (*e.g.* Eu^{+3} Tb^{+3}), Uranyl ions (UO^{2+}), lanthanide ion-doped glass (*e.g.*, with Mn, Cu, Nd, Sn, Ce, Ag), and crystals (ZnS, CdS,).
3- Organometallic compounds – Include ruthenium complexes (*e.g.* Ru (bi $Py)_3$), complexes containing chelating agents (*e.g.* 8- hydroxyquinoline) and complexes containing lanthanide ions.

The operations of Organic LEDs (OLED) and inorganic LEDs are very easy and simple. The electrons and the holes are injected in the "active" region, where they recombine, thereby causing a photon emission. The electrons are injected into the conduction band of a suitable organic material, while holes are injected in the valence bond. These carriers are diffused and they meet and recombine for forming excitons. Thereafter, these excitons decay to their ground state, which further results in photon emission. A similar process is used in fluorescence, however, in this case, it is induced by electricity and known as electroluminescence.

ElectroLuminescence (EL) is an electricity-driven radiative emission procedure. This phenomenon is noted in many traditional semiconductors. It was first observed by Destriau in 1936 when they used inorganic compounds (ZnS phosphors) [1]. In 1947, it was noted that transparent anodes can be developed after depositing an Indium Tin Oxide (ITO) layer on the glass surface. This discovery could be used for acquiring light emitting planar surfaces [2]. Many of the aromatic organic molecules display photoluminescence, and hence, can be used as electroluminescent material. In 1963, Pope *et al.* [3] first noted EL when they used organic semiconductor material. Many of the earlier researchers stated that the combination of injected electrons from Electrode 1 and holes from Electrode 2 played a vital role during the light emission strategy. In 1983, EL was noted in poly (vinyl carbazole) [4], which encouraged other researchers to search for different electroluminescent materials existing in the other visual spectrum range. However, the researchers were unable to develop organic EL devices since these devices showed a lower efficiency and a poor lifetime.

In 1987, a group of researchers working in Kodak used 2-layered OLEDs to design a device that showed better EL efficiencies and lower operational voltages, when they investigated small molecular structures and materials [5]. They noted that a single anthracene crystal, which was ten micrometres thick, showed an emission when they used silver paste electrodes. A large voltage value (*i.e.*, 400 V) was needed for generating emission. Similar results were noted by Helfrich and Schneider [6] when they used liquid electrodes. Furthermore, in 1987, another research team at the Eastman Kodak Research Laboratories developed an EL diode that displayed good characteristics [7]. They selected organic semiconductors rather than inorganic semiconductors to develop their novel device, which resembled a traditional p-n diode. Thus, they could generate an intense EL, despite using a low voltage.

In 1982, Vincett *et al.* [8] observed a blue EL when they sublimed anthracene on oxidised aluminium and used it as an electrode, while the second electrode was formed after thermally evaporating the semi-transparent gold. They could decrease the voltage value significantly to 12 V. The OLEDs are not necessarily manufactured in the semiconductor factories, unlike LEDs. Also, they are not restricted to smaller sizes. The organic LEDs are developed using a cost-effective printing line, like that needed for semi-transparently printing a newspaper, which helps in achieving a higher resolution of the display, which consumes little power. OLEDs show a better performance, like a high contrast ratio, higher luminance efficiency, wide viewing angle, and rapid response time. Additionally, the Active-Matrix OLED (AMOLED) displays were seen to be self-illuminating and do not need a back-light source, which results in thin display devices. These displays are used in many mobile applications like tablets, laptops and cell phones.

One important and unique property displayed by OLEDs was their flexibility. Thus, these devices can endure some mechanical deformation like rolling, bending or folding, without any effect on their performance. The OLED devices are categorised into 2 types based on the organic layer which is used in the devices:

1- Small molecular devices (SMOLED)
2- Organic polymer devices (PLED or LEP)

The SMOLED devices can be fabricated using different vacuum evaporation methods, while the polymeric structures are either adhered to using ink-jet printing or spin casting techniques. The small-molecule technology was first developed and commercialised at the Eastman Kodak Co. (Rochester, NY). The PLEDs were developed in 1990 by the research team at Cambridge University and have undergone many recent advancements. A general SMOLED device

CHAPTER 4

Multicomponent Approach for the Synthesis of Xanthenes

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Abstract: Xanthenes are known to exhibit a diverse range of biological properties, such as antimicrobial, antitumor, antioxidant, antimalarial anti-inflammatory, *etc*. Owing to their significant applications in medicinal as well as industrial fields, the xanthene framework has appeared as a remarkable synthetic target. This chapter offers an overview of the plethora of multicomponent reactions employed for the synthesis of xanthene and its derivatives. Multicomponent reactions that comply with the "Green Chemistry" principles have emerged as a powerful strategy that combines structural diversity with eco-compatibility.

Keywords: Catalysis, Green Chemistry, Heterocycles, Heterogeneous Catalysts, Ionic Liquids, One-pot Synthesis, Multicomponent Reactions, Xanthene.

INTRODUCTION

Xanthenes (dibenzo[*b,e*]pyrans) (Fig. **1**) are vital biologically dynamic molecules with diverse imperative pharmacological properties such as antiviral [1], anti-inflammatory [2], antimycobacterial [3], antioxidant [4], antiproliferative [5], antileukemic [6], antifungal [7] and antiplasmodial [8], *etc.* Owing to their interesting spectroscopic properties, these heterocyclic moieties have also been utilized as dyes [9], sensitizers in photodynamic therapy [10] and laser technology [11], as well as pH-sensitive fluorescent materials [12].

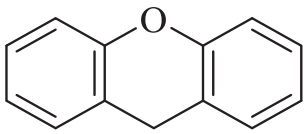

Fig. (1). Structure of 9*H*-Xanthene/ dibenzo[*b,e*]pyran

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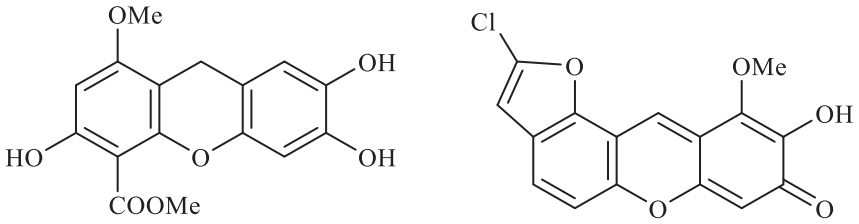
Xanthene and its derivatives are generally synthesized or obtained as a microbial metabolite. They are seldom isolated from natural plants; for instance, Blumeaxanthene (I and II) [13, 14] is extracted from the stem of Blumea riparia (Bl.) DC. (Fig. **2**).



Bluemexanthene I Bluemexanthene II

Fig. (2). Example of Natural Xanthenes

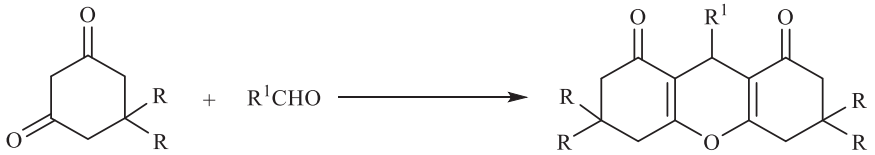
The unique properties of xanthene make its synthesis a perpetual field of research [15 - 18]. In recent years, there have been prodigious advancements in "Green Chemistry," which accentuates the design and development of environmentally benevolent protocols to access biologically elaborated molecular scaffolds. The use of multicomponent approach for the synthesis of heterocyclic compounds is a step forward towards sustainability. Multicomponent reactions have well-known advantages like simplicity, efficiency, selectivity, low-energy consumption, high atom economy, low-waste production [19 - 23]. To further influence and improve the environmental performance of organic synthesis, the combination of multicomponent reactions with other Green chemistry tools, like nonconventional solvents/energy media, application of heterogeneous catalysts, catalyst-free, and solvent-free approaches, are also extensively explored by the chemical community. In this perspective, the utility of multicomponent reactions for the green synthesis of xanthene has been highlighted in this chapter.

Synthesis of 1,8-Dioxo-octahydroxanthenes by Condensation of Cyclohexane-1,3-diones with Aldehydes

Various reaction conditions have been explored for the synthesis of 1,8-diox--octahydroxanthenes **3** *via* condensation of aldehydes **2** and 5,5-dimethyl cyclohexane-1,3-dione (dimedone) **1a**/cyclohexane-1,3-dione **1b** (Scheme **1**).

Ionic liquids with Brønsted acidic property, like 1,3-bis(4-sulfobenzyl)-1*H*-imidazol-3-ium hydrogen sulphate [24], ethylammonium *N*-sulfonic acid chloride ($[CH_3CH_2NH_2SO_3H]Cl$) [25], 1,10-butylenebis(3-sulfo-3*H*-imidazol-1-ium)

chloride (BBSIC) [26], triethyl ammonium dihydrogen phosphate ($[Et_3NH]H_2PO_4$) [27], 1,1′-disulfo-[2,2′-bipyridine]-1,1′-diium chloride ($[BiPy](SO_3H)_2Cl_2$) [28], *N*,*N*-diethyl-*N*-sulfoethanammonium chloride [29], 1,3-disulfonic acid imidazolium chloride ([Dsim]Cl)/3-methyl-1-sulfonic acid imidazolium hexafluorophosphate(V) ($[Msim]PF_6$)/ 3-methyl-1-sulfonic acid imidazolium tetrafluoroborate ($[Msim]BF_4$) [30], triethylammonium hydrogen sulfate ($[Et_3NH]HSO_4$) [31], 1-methylimidazolium triflouroacetate ([Hmim]TFA) [32], 1-carboxymethyl-3-methylimidazolium tetrafluoroborate ($[Cmmim]BF_4$) [33], poly(4-vinylpyridinium butane sulfonic acid) hydrogen sulfate ($P(4VPBSA)HSO_4$) [34], *N*-sulfonated 1,4-diazabicyclo[2.2.2]octane ($[DABCO](SO_3H)_2(Cl)_2$) [35], 1,3-disulfonic acid imidazolium hydrogen sulfate (DSIMHS) [36], 1,1,3,3-tetramethylguanidine (TMGT) [37], bis-2,3,4,6,7,8,9,1--octahydropyrimido[1,2-*a*]azepinium-ethyl disulfate ($[DBU]_2EDS$) [38], $[Bmim]BF_4$/ 3-carboxymethyl-1-methylimidazolium bisulfate ($[Cmim]HSO_4$)/ 1-methyl-2-pyrolidonium hydrogen sulfate ($[NMP]HSO_4$)/ $[Bmim]HSO_4$/ 1-(--sulfonic acid)butyl-3-methylimidazolium hydrogen sulfate ($[(CH_2)_4SO_3Hmim]HSO_4$)/1-butyl-3-methylimidazolium dihydrogenphosphate ($[Bmim]H_2PO_4$) [39], and 3-(*N,N*-dimethyldodecylammonium)propane sulfonic acid hydrogen sulfate ($[DDPA]HSO_4$) [40], $[Hbim]BF_4$ [41], were employed for the synthesis of 1,8-dioxo-octahydroxanthenes through one-pot condensation of various aldehydes with dimedone or cyclohexane-1,3-dione (Scheme **1**,Table **1**).



Scheme. (1). Synthesis of 1,8-dioxo-octahydroxanthenes by condensation of cyclohexane-1,3-diones with aldehydes.

Table 1. Synthesis of 1,8-dioxo-octahydroxanthenes by condensation of cyclohexane-1,3-diones with aldehydes catalyzed by ionic liquids.

Reaction Conditions	Examples	% Yield	Time (min.)	Reference
BAILS, 95-100°C	13	85-95	30-45	[24]
$[CH_3CH_2NH_2SO_3H]Cl$,120°C	15	58-90	15-55	[25]
BBSIC,100°C	10	67-92	10	[26]
$[Et_3NH]H_2PO_4$, 100°C	10	84-95	5-30	[27]

CHAPTER 5

From Atoms to Macromolecules: 100 Years of Polymer Research

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Abstract: In March 1920, Professor Hermann Staudinger coined the term "macromolecules" to explain the physicochemical behavior of different synthetic and natural polymers. Far from the skepticism of the scientific community, other researchers, such as Wallace Carothers, were able to explain not only the synthesis but also the chemical nature of synthetic polymers by considering Staudinger´s ideas. The Nobel Prize awarded to Staudinger in 1953 is one of the milestones of a new era in which polymers and polymer science would certainly change the world. In this review, the historical evolution of polymer chemistry and that of different synthetic methods to produce polymers with well-defined molecular architectures are discussed. Different synthetic methods are reviewed, from classical (ionic, condensation, and coordination) to recent ones (reversible activation/deactivation using nitroxides, transfer agents or metal complexes, conducting polymers, and meta thesis polymerization). This review is expected to be of interest not only to those involved in polymer science but also to others interested in the development of synthetic chemistry.

Keywords: Free radicals, Historical background, Initiators, Ionic, Macromolecules, Metallocenes, Metathesis, Polycondensations, Polymers, Polyolefins, Reversible deactivation/activation polymerizations.

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INTRODUCTION

Although polymers and macromolecules are an essential part of our nature and have been commonly used since humans appeared in the world until 1930, understanding of their physicochemical nature and behavior has not yet been well established. At the beginning of the 20th century, chemists supported a common idea regarding the strange behavior and nature of polymeric substances: they must be colloidal aggregates formed by the interaction of intermolecular forces of mysterious origin. As soon as these forces strengthened, viscosity, long-range elasticity, and high strength properties appeared. This idea was so widespread among the chemical community that when Hermann Staudinger proposed the existence of giant molecules instead of colloidal aggregates, one of his colleagues, Prof. Heinrich Wieland, tried to convince him to drop his idea since "o*rganic molecules with a molecular weight greater than 5000 do not exist…."* Fortunately, Staudinger did not abandon his revolutionary hypothesis: not only did he succeed Wieland as Head of the Chemisches Laboratorium at the University of Freiburg, but he also was awarded the Nobel Prize in Chemistry 1953 for his seminal contribution to the nature of macromolecules.

Staudinger's hypothesis and his outstanding contribution were soon recognized by the scientific community in the following decades. Like Staudinger, Giulio Natta and Karl Ziegler (1963), Paul Flory (1974), Pierre-Gilles De Gennes (1991), Alan G. Mac Diarmid, Alan J. Heeger and Hideki Sirakawa (2000), John Bennett Fenn, Koichi Tanaka, and Kurt Wüthrich (2002), and Robert Grubbs, Richard Schrock and Yves Chauvin (2005) also won the Nobel Prize in Chemistry for their research and developments leading to an understanding of the behavior of macromolecules. And we can expect more Nobel laureates in the coming years since polymer science seems to be an endless source of new ideas and theories.

Throughout this chapter, readers will be able to dive into the history of polymer science, its achievements, and its heroes. The text will focus on some of the main advances developed during this first century, following their historical sequence and considering their milestones. Besides the facts inherent to chemistry, which will be considered but are not the focus of this review, the main purpose of the text is to provide information on the history of polymer science. The focus will be on the milestones reached during this first century, acknowledging the research and development of polymer chemists worldwide. In addition, we will be delighted to invite readers to picture a more prolific, brilliant, and fascinating era in this amazing field of science.

POLYMERS AND MACROMOLECULES: HISTORICAL BACKGROUND

In 1832, the Swedish chemist Jöns Jakob Berzelius introduced the term *isomer* (from the Greek *isos* meaning "equal" and *meros* meaning "part") to describe substances having identical composition but differing properties [1]. Later, in 1833, Berzelius presented the term *polymer* (from the Greek *polys* meaning "many" and *meros* meaning "part") as a special type of isomerism [1, 2]. He recognized that two compounds may have the same composition yet differ in molecular weight. In other words, the term *polymerism* was attributable to two substances having identical relative compositional formulas but different absolute compositional formulas; for example, a difference in the total number of atoms present in ethylene *versus* butane [2, 3]. It was a broader definition than the one that is used currently, although it was enough to meet the demands of that time. On the other hand, Berzelius used the term *metamerism* to define two substances having identical absolute compositional formulas but different chemical properties [2 - 4].

Berzelius did not consider high molecular weight substances in his definitions, but the terms were not a challenge until the mid-19th century. Therefore, Augustus Kekulé presented a solid foundation for polymerism. In 1878, Kekulé described the tetravalency of carbon and defined the bond aspects as "*carbon atoms bound by equal parts of the affinity of the other*"; he even proposed the existence of polyvalent atoms capable of producing "*sponge or net-like*" molecular mass. Kekulé also predicted which natural organic substances may consist of elongated chains, such as proteins, starch, and cellulose, and the respective properties that should be related to the molecular structure [3].

Over the next thirty years, several researchers produced important works, which also contributed to the field of polymer science at that time. However, since 1910, History has reserved a distinct space for a brilliant researcher who made one of the most notable contributions to polymer science. We refer to Hermann Staudinger, who started studying the polymerization of isoprene [5]. The most outstanding fact, which became one of the major milestones of polymer science, was presented by Staudinger in 1920 in his famous article *"Über Polymerisation,"* which in English means "On Polymerization" [6, 7].

Staudinger began his research career at the International Technical School (ETH) in Zurich, Switzerland, and later at the Albert Ludwig University in Freiburg, Germany, where the theoretical and conceptual basis of contemporary polymer science was born. Near the end of World War II, more precisely on November 27, 1944, the institute was subjected to the stupid effects inherent to wars.

CHAPTER 6

An Overview of Oxidizing and Reducing Agents in Total Synthesis

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Abstract: Synthetic organic chemists have a wide range of reagents for the alteration of functional groups in organic compounds and the choice of usage is a continuous challenge especially in the total synthesis of complex molecules. Oxidizing and reducing agents play a vital role in the total synthesis of natural and synthetic molecules having biological importance. In this chapter, we emphasize the recent development of oxidizing and reducing agents in organic chemistry and their importance in the field of synthesis. Heterogeneous nanocatalysts also emerged as powerful catalysts employed in oxidation and reduction and are studied. Definitely, oxidation-reduction in organic synthesis is an odyssey and it has ample association with stereoselectivity, synthetic methods, catalysis, and green chemistry.

Keywords: Chemical transformations, Nanocatalysts, Natural products, Oxidation, Oxidizing agents, Recent advances, Reduction, Reducing agents, Synthetic organic chemistry, Total synthesis.

INTRODUCTION

Natural products have been incessantly contributing to various drugs used for the treatment of several human diseases [1, 2]. Nevertheless, incising for the optimal drugs has been always formidable and intriguing because of the complexity of structural modifications. In this aspect, effectual and flexible chemical synthesis approaches to the pertinent molecules can provide diverse opportunities. Total synthesis may be defined as the synthesis of target molecules from available starting materials which can be generally applied to natural products [3, 4]. Total synthesis is always challenging due to its complexity. In synthetic organic chemi-

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stry, oxidation and reduction are the two important pathways for chemical transformations [5, 6].

These reactions are extremely useful in synthetic organic chemistry, pertaining total synthesis of natural products, materials, pharmaceutical molecules, *etc*. We can say sturdily that without oxidation or reduction reaction, there is no practical total synthesis.

Oxidation

Oxidation of alcohols affords ketones or aldehydes, and oxidation of aldehydes generally gives carboxylic acids, as shown in Fig. (**1**), where [O] indicates that the reaction is oxidation.

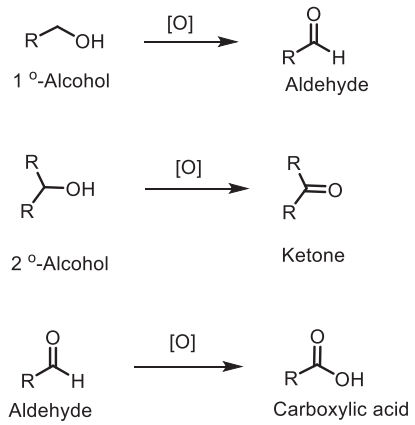

Fig. (1). General oxidation transformations.

In the first two reactions, there is a "loss of H" whereas, in the third reaction, there is a replacement of an H on C by O with a "gain in O".

The oxidation of primary alcohol to an aldehyde is a fundamentally important reaction arrayed in academic and industrial settings to access versatile chemical building blocks, synthetic intermediates, and final targets. Amongst the horde of reagents and conditions available to perform this functional group transformation, selectivity (*i.e.,* avoiding over-oxidation) and versatility (*i.e.,* tolerance of other functional groups) are the two important measurements.

One of the most common transformations in organic synthesis is the oxidation of the hydroxy group, and although certain procedures remain prevalent, there is a constant need to develop new systems. Historically, one-step alcohol oxidations to aldehydes have relied heavily on chromium reagents (*e.g.* pyridinium chlorochro-

mate (PCC)), activated sulfur etiquettes (*e.g.* Swern and Corey–Kim), and manganese compounds (*e.g.* MnO_2) [7 - 10]. More recently developed methods include hypervalent iodine compounds (*e.g.* Dess–Martin periodinane (DMP) followed by 2-iodoxybenzoic acid (IBX) and nitrosyl radicals (*e.g.* (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO). Additionally, molecular oxygen-based methods using transition metals [11] have also been developed. On balance, however, the mainstay protocols that lead to the one-step alcohol oxidation scenery are Swern [12], IBX/DMP [13, 14], TEMPO [15, 16], and Ley–Griffith oxidations [17, 18]. Recently, Sharpless epoxidation and dihydroxylation are found ubiquitous in many total syntheses [19, 20]. More recently, the supported gold/silver nanoparticles as catalysts have become significant in chemical transformations for both oxidation and reduction [21, 22].

Swern oxidation is mild and efficient but there are problems with loathsome side products and difficulties with the large-scale operation. Similarly, chromium oxidants can cause problems during the work-up of the products and disposal of the toxic residues. Therefore, alternatives to these well-tried methods are warranted but they must demonstrate clear advantages over these systems, be consistent and easy to use, and especially applicable in the organic synthesis.

Some of the Oxidizing Agents and their Applications

Tetrapropylammonium Perruthenate (TPAP)

TPAP is an easily soluble, air-stable, nonvolatile oxidant used for the oxidation of alcohols. The oxidant also known as Ley–Griffith reagent utilizes the catalyst *n*-$Pr_4N[RuO_4]$ in combination with an excess (1.5 equiv.) of the co-oxidant *N*-methylmorpholine *N*-oxide (NMO), both available commercially. Like many named reactions, alterations to the Ley–Griffith reaction have been reported (*e.g.,* Tetraphenylborate salt of *N*-methyl morpholine-*N*-oxide [NMO·TPB] and tetraphenylborate salt of diazabicyclo[2.2.2]octane *N*-oxide [DABCOO·TPB]), and have numerous applications using TPAP as a catalyst.

TPAP has advantages, like good functional group tolerance and no epimerization of α-chiral centers or double bond isomerization. However, the main drawback of TPAP is that it can cleave 1,2-diols like other metal oxidants.

Thapsigargins are complex guaianolides with strong Ca^{2+}-modulating properties. In 2004, Steven Ley *et al.* reported [23]the elegant synthesis of thapsigargins. In their synthetic approach, they successfully transformed tetraol**1** to the desired lactone **2** by TPAP oxidation in a single-step sequence (Scheme **1**).

CHAPTER 7

Amino Acid-derived Ionic Liquids: Novel Biodegradable Catalytic Systems for Green Synthesis of Heterocycles

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Abstract: The Amino Acid-derived Ionic Liquids (AAILs), as green biodegradable catalysts, gained special attention in recent years due to their alignment with green chemistry's important rules. They could be prepared *via* easy techniques. Ohno and co-workers synthesized amino acid-derived ILs for the first time. AAILs could play multiple roles as solvents and/or excellent promoters with high catalytic activity and also as chiral additives. The special advantages of AAILs usage are *i*) elevation of the product yields, *ii*) excellent chemo and/or stereo-selectivity, *iii*) short reaction times, *iv*) simple work-up procedures, *v*) diminishing or prevention of by-products formation, *vi*) mild reaction conditions, and *vii*) recoverability and reusability within several cycles without noticeable activity loss. The synthesis of pharmaceutically-active heterocycles is interesting in organic chemistry and medicinal fields. The multi-activity characteristics of AAILs make them interesting candidates for promoting different classes of MCRs to prepare heterocyclic compounds.

In the book chapter, the applications of various AAILs (alone or as a part of core-shell structures) will be discussed for the synthesis of heterocycles with a glance at nano and green chemistry. The content of the chapter has been divided into two main parts, which are a) the applications of AAILs as catalysts and/or solvents in the synthesis of heterocycles, and b) employing the bionanocomposites that included AAILs as catalysts in the synthesis of heterocycles. According to the reports, they played a key role in obtaining different libraries of heterocycles, which could potentially be active drugs.

Keywords: Amino Acids (AAs), Amino Acid-Derived Ionic Liquids (AAILs), Catalyst, Chiral Ionic Liquids (CILs), Ionic Liquids (ILs).

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INTRODUCTION

Ionic liquids (ILs) are organic/inorganic salts in a liquid state with a melting point below 100 °C (212 °F). Moreover, ILs or molten salts are defined as liquid compounds that show ionic-covalent crystalline structures. They illustrate many special properties, for example, environmental benignity, good thermal and chemical stabilities, low vapor pressure, low toxicity, high ion density and ionic conductivity, non-flammability, variable viscosity, high solubility, wide liquid range, combustibility, reusability, *etc* [1, 2]. ILs have wide applications, including in industries, modern biology, chemistry, organic synthesis, green solvents, solid catalysts, lubricants, biomass conversion, electrolytes in batteries, fuel cells, separation science, and many other specialized areas [3 - 7]. Nowadays, they have also been utilized as chemicals, which possess antifungal, antibacterial, antimicrobial, and herbicidal activities and probably cytotoxic effects on invertebrate and vertebrate animals and other organisms [8 - 11]. It is suggested that the toxicity of ILs relies on different structural parameters, including cation and anion type, the cation alkyl side chain length, functionalized cation side moieties, the nature of cation and anion moiety, *etc*. Thus, the biological properties of synthesized ILs can be adjusted by selecting convenient anion and cation structures [12, 13]. More often, various ILs have been prepared that contain cationic parts, such as imidazolium [14], phosphonium [15], and cyclic or non-cyclic quaternary ammonium, because of their simplicity and suitability for chemical substitution [16]. ILs have an essential role as dual green solvents and/or catalysts, which are applicable immensely in synthetic organic chemistry [17, 18]. The low vapor pressure of ILs makes them an appropriate choice in green chemistry.

Amino acids (AAs) are the building blocks of proteins. They involve dual carboxylic acid and amino functional groups on the carbon adjacent to the C=O (α carbon) that help them possess both weakly acidic and basic properties. They indeed exist as a salt of ammonium cation and carboxylate anion, with different side chains. In 1806, asparagine (Asn) was the first discovered amino acid [19]. Because of bearing numerous functional groups (carboxylic acid residues, amino acid groups, and diverse side groups), they play critical roles in different domains of science and technology, such as surfactants, corrosion inhibition of metals, gas storage, metabolite and physiological applications, structuring nanoparticles, and efficient ligands in organometallic chemistry [20 - 25].

AAs are also directly applied to prepare some species, called chiral ionic liquids (CILs), which exhibit diverse properties, such as toxicity toward NIH/3T3 cells

[26], asymmetric transfer hydrogenation (ATH) of acetophenone [27], enhanced protease enantioselectivity [28], chiral molecular recognition [29], and electrophoresis [30].

Task-specific ionic liquids (TSILs) are some classes of ILs that can be designed and developed based on the user's need for the desired physical, chemical, and biological properties. A vast range of TSILs has been interpreted in different fields of science, technology, and pharmacy [31]. They also possess a highlighted role as catalysts and/or solvents in organic synthesis [32].

In fact, the accessibility of AAs as both cations and anions causes the natural AAs to act as a platform as favorable candidates for "task-specific" functional ILs [33]. Ohno and co-workers, in 2005, synthesized some TSILs from the direct combination of 20 natural amino acids and imidazolium cations [34]. It is noteworthy that different kinds of CILs have previously been obtained from amino acid-based precursors [35], but it is the first report on the synthesis of amino acid-based ILs (AAILs) consisting of an organic counter ion. The obtained AAILs by Ohno generally demonstrated thermal stability up to 200 °C and low to moderate ionic conductivity related to the utilized amino acid. The conductivity is in a linear correlation with glass transition temperature (Tg) measurements. The Kou group has also prepared some classes of AAILs consisting of the amino acids or amino acids esters, as the acidic cationic part ([AA]X and [AAE]X). These chiral, non-toxic, and even natural materials are called "fully green" ILs [36].

Besides all the expectant properties of ILs, AAILs possess special properties, such as low cost, high hydrogen-bonding ability, good thermal stability, reduced toxicity, multi-functionality, chirality, biodegradability, and high biocompatibility [37]. Actually, AAILs are a class of CILs derived from various chiral amino acids, which are renewable raw materials. AAILs demonstrated a vast range of applications in various fields, such as surfactants [38], chiral organocatalysts [39], environmental applications for heavy metal removal [40], anticorrosive and lubricating additives [41], pharmacology and drugs [42], chiral extractions and chromatographical separations [43], and CO_2 absorptions [44].

The biodegradability of the various classes of ILs has gained special attention in more green synthetic chemistry [45, 46]. Many reports also introduce AAILs as biodegradable materials [47]. Although the biodegradation analysis data of ILs and AAILs are rare [48], and the toxicity of these compounds from some special environmental aspects is also a subject of discussion [49], they are generally known as bridgeable catalysts in comparison to many other catalytic species in the field of chemistry.

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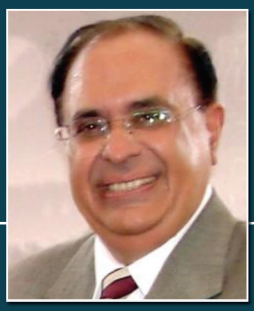

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Prof. Atta-ur-Rahman, Ph.D. in Organic Chemistry from Cambridge University (1968) has 1,232 international publications (45 international patents and 341 books). He received the following awards: Fellow Royal Society (FRS) London (2006), UNESCO Science Prize (1999), Honorary Life Fellow Kings College, Cambridge University (2007), Academician (Foreign Member) Chinese Academy of Sciences (2015), Highest Civil Award for Foreigners of China (Friendship Award, 2014), High Civil Award Austria ("Grosse Goldene Ehrenzeischen am Bande") (2007), Foreign Fellow Chinese Chemical Society (2013), Sc.D. Cambridge University (UK) (1987), TWAS (Italy) Prize (2009). He was the President of Network of Academies of Sciences of Islamic Countries (NASIC), Vice President TWAS (Italy), Foreign Fellow Korean Academy of Science & Technology, President Pakistan Academy of Sciences (2003-2006) and (2011 – 2014). He was the Federal Minister for Science and Technology of Pakistan (2000 – 2002), Federal Minister of Education (2002) and Chairman Higher Education Commission/Federal Minister (2002-2008), Coordinator General of COMSTECH (OIC Ministerial Committee) (1996-2012), and the Editor-in-Chief of Current Medicinal Chemistry.