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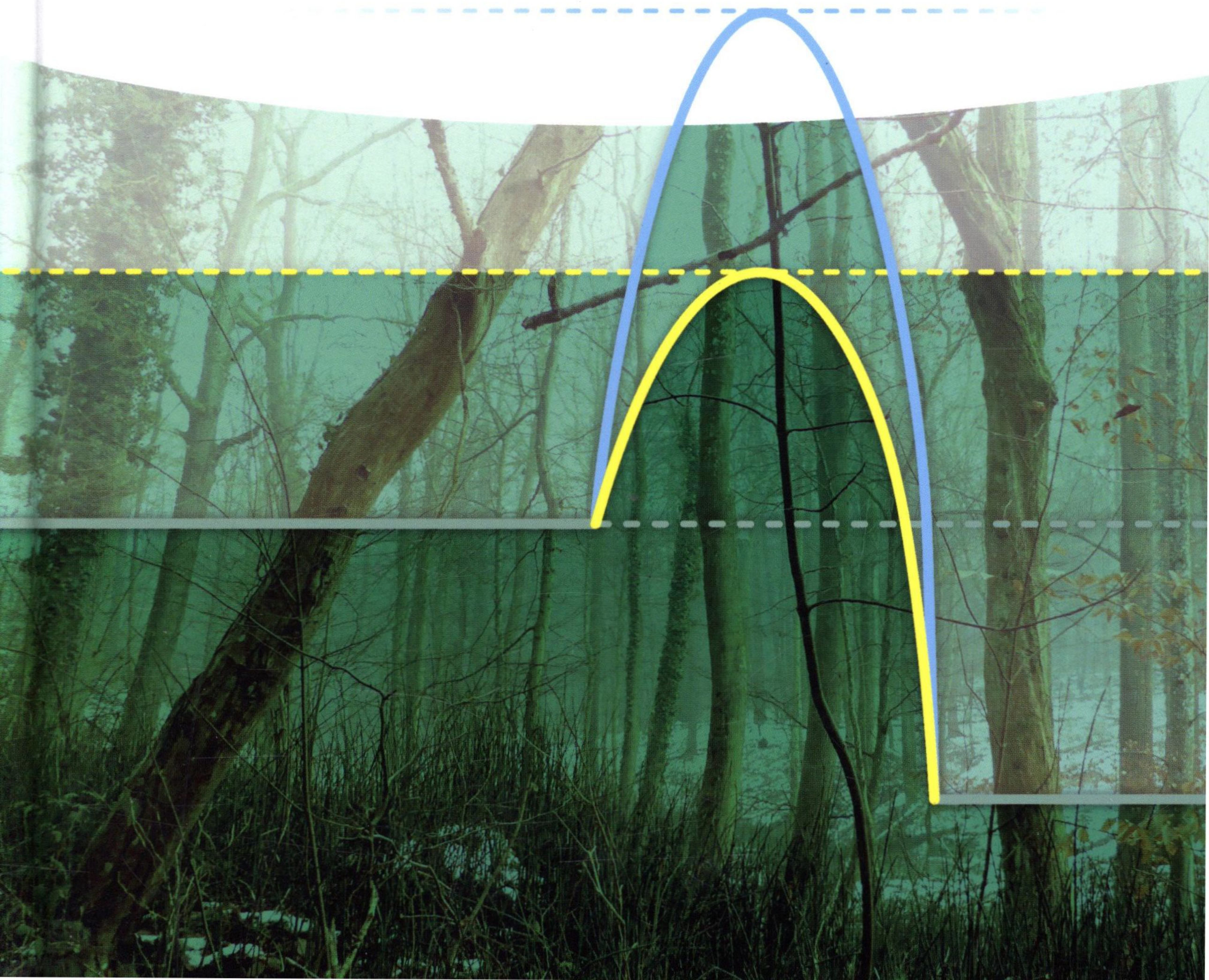
Edited by Rafael Luque and Frank Leung-Yuk Lam

Sustainable Catalysis

Energy-Efficient Reactions and Applications



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Highlighting sustainable catalytic processes in synthetic organic chemistry and industry, this useful guide places special emphasis on catalytic reactions carried out at room temperature.

It describes the fundamentals, summarizes key advances, and covers applications in industrial processes in the field of energy generation from renewables, food science, and pollution control. Throughout, the latest research from various disciplines is combined, such as homogeneous and heterogeneous catalysis, biocatalysis, and photocatalysis. The book concludes with a chapter on future trends and energy challenges for the latter half of the 21st century.

With its multidisciplinary approach this is an essential reference for academic and industrial researchers in catalysis science aiming to design more sustainable and energy-efficient processes.

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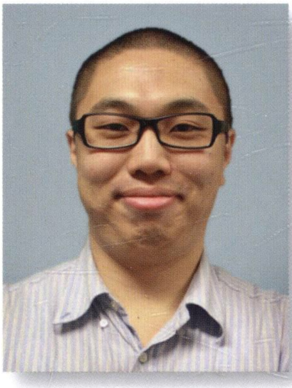

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ISBN 978-3-527-33867-2

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www.wiley-vch.de

Luque • Lam (Eds.)

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Library of Congress Card No.:
applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at http://dnb.d-nb.de.

Print ISBN: 978-3-527-33867-2
ePDF ISBN: 978-3-527-69301-6
ePub ISBN: 978-3-527-69302-3
Mobi ISBN: 978-3-527-69304-7
oBook ISBN: 978-3-527-69303-0

Cover Design Formgeber
Typesetting SPi Global, Chennai, India
Printing and Binding C.O.S. Printers Pte Ltd Singapore

Printed on acid-free paper

Sustainable Catalysis

Contents

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Introduction to Room-Temperature Catalysis

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1.1 Introduction

The world's energy demand is expected to increase significantly in the coming years as a result of the exponential economic growth of emerging countries, BRIC (Brazil, Russia, India, and China). Such an increased energy request is closely associated with environmental concerns and deficiency in water supply. These key challenges should be addressed by creating and maintaining conditions that allow humans and nature to exist in productive harmony. Only such a sustainable direction will permit fulfilling the social, environmental, and economic requirements of present and future generations and avoid the world passing the point of no return [1].

Chemistry has always played a pivotal role in development of societies by improving the quality of life, the lifespan, and so on. However, despite its many important progresses, chemistry is often recognized more as a problem than as the solution to our daily needs. Indeed, the task of changing the persisting vision that society and governments uphold about chemistry is one of the biggest challenges of chemists for the 21st century; this challenge should start from the design and development of benign and efficient manufacture protocols. To improve chemical production efficiency and fulfill international legislation, a multidisciplinary approach aimed at reducing by-products/waste, optimizing energy utilization, controlling emissions (climatic change), and using renewable materials to avoid hazardous or toxic substances is mandatory. In this connection, the "Green Chemistry" concept, being a list of 12 principles, is one of the most exciting, innovative, and realistic approaches that has emerged in order to minimize the drawbacks of chemical processing and contribute to the protection of the environment [2]. "Green Chemistry" advocates increasing research on new renewable feedstocks, environmentally benign solvents (preferably water), catalysis, and greener technologies, processes, and products. Among the "Green Chemistry" principles, the ninth, focused on catalysis, plays

Sustainable Catalysis: Energy-Efficient Reactions and Applications,
First Edition. Edited by Rafael Luque and Frank Leung-Yuk Lam.

a key role in certifying the world's sustainability by improving processes in the chemical industry, making them more efficient and benign. The development of greener catalytic protocols through the rational design of new catalysts, both homogeneous and heterogeneous, as well as solvent choice is important as it will increase valuation and understanding at the government level and in society.

A "catalyst" is a substance that increases the rate at which a chemical reaction proceeds without itself becoming permanently involved. There are many fundamental parameters in a chemical reaction that can be controlled by selecting the appropriate catalyst, including, for example, energy consumption, selectivity, productivity, and atom economy. Accordingly, the development of new catalysts or catalytic systems can be considered as an important step toward establishing a more green and sustainable chemical industry. In this regard, the design of more effective catalysts and catalytic protocols that allow a chemical process to be carried out at room temperature is a highly beneficial way to minimize both the energy demand and the risk (minimizing safety issues) for employees of a chemical plant. Furthermore, by decreasing the reaction temperature, the selectivity toward the desired product normally increases, thereby minimizing undesired side reactions and by-products. On the other hand, the reaction kinetics can be significantly hampered at room temperature and the catalyst should therefore be selected carefully to provide a system having a sufficiently low activation energy that allows the reaction to proceed at an acceptable rate without auxiliary energy input. Such selected catalysts for room-temperature reaction protocols can be both homogeneous (e.g., organometallic complexes, ionic liquids) and heterogeneous (e.g., metal nanoparticles, supported nanoparticles). Recently, excellent reviews by Lam and Luque have covered this topic in detail [3].

The aim of this chapter is to provide an overview and point out some of the most relevant catalytic systems that allow carrying out catalytic reactions at room temperature. The catalytic systems will be divided in two main groups depending on the nature of the catalyst involved, namely, (i) ionic liquids and (ii) homogeneous and heterogeneous catalyst-containing transition metals from groups 9 to 11 of the periodic table.

1.2 Room-Temperature Homogeneous Catalysts

Homogeneous catalysts are often superior to heterogeneous ones in terms of activity and, in particular, selectivity. In addition, the reaction conditions (temperature, pressure, etc.) are usually milder. However, homogeneous catalysis is hampered by other important issues from an industrial or applicability point of view, such as catalyst recovery and recyclability.

1.2.1 Ionic-Liquid-Based Catalytic Systems at Room Temperature

Ionic liquids are defined as salts only composed of ions, which melt without being decomposed. A special group of ionic liquids are the so-called room-temperature ionic liquids, which are liquid below 100 °C. The first known ionic liquid (ethanolammonium nitrate) was reported in 1888 by Gabriel and Weiner [4]. Later in 1914, Walden reported the synthesis of other ionic liquids

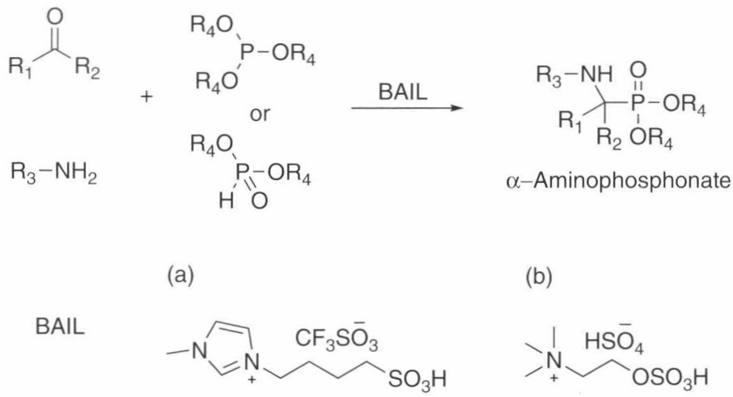

Figure 1.1 Brønsted acidic ionic liquids (BAILs) used as catalyst in the synthesis of α-aminophosphonates in a one-pot, three-component reaction. (Adapted with permission from Ref. [8]. Copyright (2014) Wiley.)

such as, for example, ethylammonium nitrate [5], but it was only in 1943 that the term "ionic liquid" was coined by Barrer [6]. In the 1970s to the 1990s, novel ionic liquids were developed and studied by US military researchers to be applied mainly as electrolytes in batteries [7]. In the past 15 years, ionic liquids have become of great importance for scientists due to their unique properties, mainly their low vapor pressure, solubility, easy functionalization (task-specific ionic liquids), and their successful applications in catalysis, nanoparticle stabilization, electrochemistry, medicine, analytical methods, benign reaction media, and so on. One main advantage of ionic liquids is the huge pool available. In principle, this allows the possibility of selecting just the right ionic liquid for a specific application. In catalysis, the selection of the ionic liquid is determined mainly by solubility characteristics (providing often biphasic systems that allow the recovery of the employed catalyst), intrinsic catalytic properties, as well as their thermal and chemical stability. Here, we overview some reactions that are conducted at room temperature in the presence of ionic liquids as catalyst and/or reaction media.

An important subgroup of ionic liquids are the so-called acidic ionic liquids, where a Brønsted or Lewis acid functionality is part of the ionic liquid ions. They have been used to replace traditional mineral acids ($MeSO_3H$, H_2SO_4, HF) or traditional Lewis acids ($AlCl_3$, $FeCl_3$) successfully and, often, with superior performance. In organic synthesis, the acidic ionic liquids have been extensively used and numerous reports have come out in the past years concerning their use as solvents or catalysts at room temperature. Since it is not possible to survey all these applications, representative examples will be pointed out to show the potential of the acidic ionic liquids in organic synthesis.

α-Aminophosphonates are compounds of great interest due to their biological and chemical applications (antibacterial, antitumor, antiviral, enzyme inhibitors). The synthesis of these compounds is normally carried out through the so-called Kabachnik–Fields reaction in the presence of a dehydrating agent and a Lewis acid. In 2009, Akbari and Heydari used a Brønsted acidic ionic liquid (BAIL) (Figure 1.1a) as catalyst instead of the Lewis acid for the synthesis of α-aminophosphonates through a one-pot, three-component (phosphite, aldehyde or ketone, and amine) reaction [9]. They got excellent results in terms of yield (up to 98%) in short reaction times at room temperature. Furthermore, the employed BAIL catalyst could be recovered and reused up to six times without any deactivation. In 2010, Fang *et al.* prepared a series of "halogen-free" BAILs to be tested as catalysts in the same reaction and obtained good results at room temperature in aqueous media [10]. In 2014, Peng *et al.* prepared a different BAIL based on the choline cation (Figure 1.1b), also to be used as catalyst in the same one-pot, three-component reaction. They claimed that their synthesized choline-based BAIL was cheaper and less toxic than the one previously reported by Akbari and Heydari [9]. Excellent results were obtained under solvent-free conditions at room temperature in short time reactions with isolated yields up to 95%. The recyclability of the catalyst was also tested up to six times without any decrease in activity or degradation of the BAIL [8].

In a recent work, Ying *et al.* [11] showed the effectiveness in terms of activity and recyclability of using multiple-acidic ionic liquids as catalysts for the synthesis of α-aminophosphonates at room temperature under solvent-free conditions. The same authors used the multiple-acidic ionic liquids in the synthesis of bis-indolylmethanes (Figure 1.2), compounds with biological activity and of great interest in the medical chemistry, under solvent-free conditions and at room temperature. Among the applied multiple-acidic ionic liquids, [TEOA][HSO_4] (triethanolammonium hydrogensulfate) showed the best performance, giving the products in excellent yield (up to 90%) after a few minutes of reaction. In addition, the catalytic system was reused up to five times without showing any sign of deactivation [12].

The protection of hydroxyl groups is an essential task in organic synthesis to avoid unwanted reactions where, for example, Grignard or alkyllithium reagents are involved. In this connection, acidic ionic liquids have shown to be alternatives to commonly used volatile organic solvents in the protection of alcohols at room temperature with excellent yields in less than 5 min reaction, making the overall process safer and greener [13]. The esterification of carboxylic acids with alcohols is a reaction of great interest because it yields esters that are valuable intermediates in the chemical industry. Chloroaluminate-based acidic ionic liquids, as substitutes of inorganic acids, were first tested in the esterification reaction by Deng *et al.* [14]. The authors highlight two main advantages of using

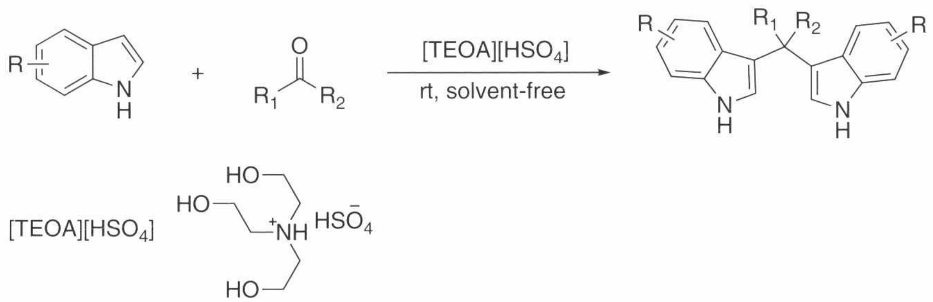

Figure 1.2 Multiple-acidic ionic liquids in the synthesis of bis-indolylmethanes. (Adapted with permission from Ref. [12]. Copyright (2014) Elsevier.)