Environmental Chemistry for a Sustainable World

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# Hydrogen Production and Remediation of Carbon and Pollutants

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# Environmental Chemistry for a Sustainable World

## Volume 6

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# Preface

## Genes Hydro

Society growth during the last century has almost entirely relied on the carbon economy, that is, the use of fossil fuels for energy and materials. The carbon economy has provided and will still provide many benefits. However, the increasing use of

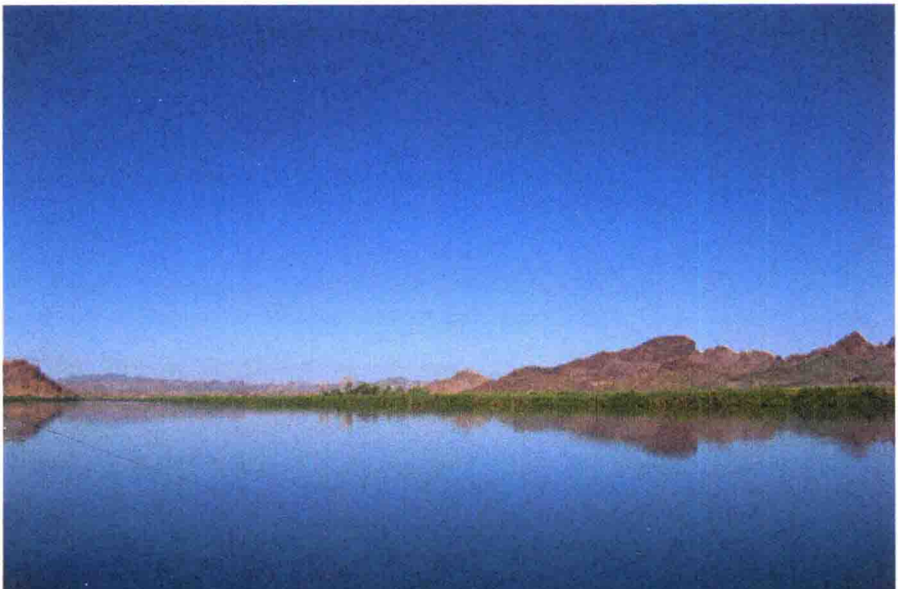

**Fig. 1** Water as a symbol of life. Colorado River, Picacho State Recreation Area, Winterhaven (Copyright: 2014 Eric Lichtfouse)

fossil fuels is partly responsible for the increase of atmospheric $CO_2$ concentrations and, in turn, global warming. There is therefore an urgent need for cleaner fuels based upon renewable materials and a carbon-neutral economy where each emitted $CO_2$ molecule is sequestered fast in plants, algae, soils, subsoils and sediments. Hydrogen is a potential clean energy because dihydrogen ($H_2$) combustion produces water, a safe medium. Remarkably, the term 'hydrogen' itself means 'clean energy' because it was coined by Antoine Lavoisier in 1783 from the Greek *genes* and *hydro* 'that generates water' (http://en.wikipedia.org/wiki/Hydrogen) (Fig. 1).

In the first chapter, Nielsen describes the chemistry of dihydrogen production from biomass. Quin et al. review the photocatalytic reduction of $CO_2$ in Chap. 2. The effects of higher atmospheric $CO_2$ on ecosystems and the techniques to sequester in terrestrial biomass are presented by Singh et al. in Chap. 3. El Ramady reviews the selenium cycle in ecosystems and describes the use of the plant giant reed for energy and remediation in Chap. 4. Chemical, biological and physical processes to treat water are described by Tandon and Singh in Chap. 5. Gunasekar and Ponnusami present ecological ways to dye textiles in Chap. 6.

Thanks for reading

Eric Lichtfouse is the author of the bestselling textbook *Scientific Writing for Impact Factor Journals*

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Aachen, Germany — Jan Schwarzbauer
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# Contents

# Chapter 1
# Hydrogen Production by Homogeneous Catalysis: Alcohol Acceptorless Dehydrogenation

**Martin Nielsen**

## Contents

**Abstract** The lifestyle in the modern western world is highly depending on the accessibility of energy and bulk chemicals. Energy is needed in the transportation sector, but also domestic and industrial consumptions of energy is comprehensive. Bulk chemicals are probably more important than people realize, and are fundamental for the thrive of almost all business fields. The latter include the industries of agriculture, food additives, pharmaceuticals, electronics, plastic, fragrances, and more. Today, the major source of both energy and bulk chemicals is fossil fuels, being responsible for more than 80 % of the energy supplies. The large amounts of $CO_2$ release owing to fossil fuel usage is believed to cause global warming on the

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long term, a highly undesired environmental consequence. Hence, it is of critical importance that alternative sources are developed and implemented in the society. One suggested solution for the energy sector is the application of a *hydrogen economy*, which transform the chemical energy in water and/or biomass into hydrogen. Considered as an energy carrier, hydrogen is then transported to the site of use where fuel cells convert its chemical energy into electricity.

Here, we review the progress in hydrogen production from biomass using homogeneous catalysis. Homogeneous catalysis has the advance of generally performing transformations at much milder conditions than traditional heterogeneous catalysis, and hence it constitutes a promising tool for future applications for a sustainable energy sector. In particular, only alcohol containing substances are covered. As such, alcohol acceptorless dehydrogenation (AAD) is the main topic of this review. Moreover, it is more easily investigated for eluding mechanistic property.

This review is divided up in four main chapters according to substrates. The first chapter, Model Substrates, describes the development of alcohol acceptorless dehydrogenation using substrates that can be categorized as model substrates. This includes e.g. isopropanol. The second chapter, Substrates with Synthetic Applications, deals with synthetic applications of alcohol acceptorless dehydrogenation. The third chapter, Biorelevant Substrates, concentrates on the use of alcohols such as ethanol, which are biomass related. The topic is alcohol acceptorless dehydrogenation reactions for both $H_2$ production and the concurrent synthetic application. Finally, Chap. 4, Substrates for $H_2$ Storage, is focusing on the use of alcohol acceptorless dehydrogenation of alcohols relevant as future $H_2$ storage molecules. This is in particular methanol.

**Keywords** Hydrogen • Sustainability • Alcohols • Acceptorless dehydrogenation • Homogeneous catalysis

## List of Abbreviations

| | |
|---|---|
| AAD | Alcohol acceptorless dehydrogenation |
| Ampy | Aminopyridine |
| A-PNP | Acridine-phosphine, nitrogen, phosphine |
| BINAP | 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl |
| Bipy | Bipyridine |
| COD | 1,5-cyclooctadiene |
| Cp | Cyclopentadienyl |
| Cp* | Pentamethylcyclopentadienyl |
| Cyp | Cyclopentyl |
| DABCO | 1,4-diazabicyclo[2.2.2]octane |
| Dbbb | 1,4-Bis(diphenylphosphino)butane |
| Dbf | Dibenzofuran |
| Dme | Dimethoxyethane |

| | |
|---|---|
| DPEN | 1,2-diphenyl-1,2-ethylenediamine |
| Dppf | Bis(diphenylphosphino)ferrocene |
| Dppm | Bis(diphenylphosphino)methane |
| En | Ethylenediamine |
| MPV | Meerwein-Ponndorf-Verley |
| MS | Molecular sieves |
| N-ligand | Nitrogen ligand |
| OPP | Oppenauer oxidation |
| OTf | Triflate |
| PC $_{sp}$3P | Phosphine, carbon ($_{sp}$3-hybridized), phosphine |
| PCP | Phosphine, carbon, phosphine |
| P-ligand | Phospine ligand |
| PNN | Phosphine, nitrogen, nitrogen |
| PNP | Phosphine, nitrogen, phosphine |
| Ppb | Parts per billion |
| Ppm | Parts per million |
| TMEDA | Tetramethylethylenediamine |
| TOF | Turnover frequency |
| To$^{M}$ | Tris(4,4-dimethyl-2-oxazolinyl)phenylborate |
| TON | Turnover number |
| Tpy | Terpyridine |
| v/v | Volume/volume |
| wt.% | Weight% |

## 1.1 Introduction

Throughout history there has been a clear coherence between a continuous technological developing of our society and an increase in demand of energy and materials. This accounts also for the foreseeable future. This will result in a number of undesired hazardous effects on the environment, the most pronounced of which is probably global warming due to severe amount of $CO_2$ release accompanied with the burning of fossil fuels. Moreover, many industries that are fundamental for the maintaining of our current lifestyle, including healthcare and food manufacturing, depend on the exploitation of oil for achieving readily available bulk chemicals. As it is generally accepted that most oil resources are going to be depleted probably within the next 50–100 years, it is of utmost importance that alternative and sustainable procedures for the bulk chemical syntheses are realized.

Several promising candidates already exist. For example, $CO_2$ can be regarded as a C1 source, and bioethanol and glycol as C2 sources. In a similar fashion, glycerol might be a C3 source, and lignin from starch a supply for aromatic compounds, and so on. Moreover, much research is already focusing on transforming e.g. bioethanol and sugar into either fuels or bulk chemicals. However, most of these technologies

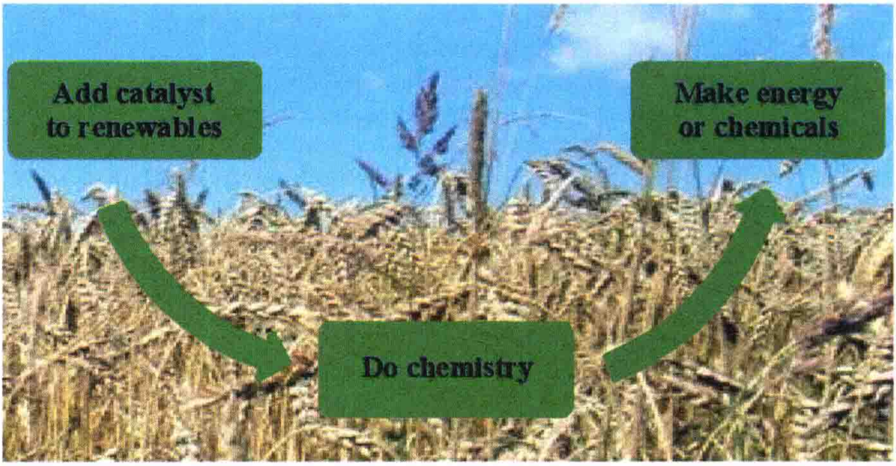


**Fig. 1.1** Illustrated principle of transforming renewable biomass into products and energy

are still in their infancy, and as such they do need considerable investigations before they are realizable on the market.

For the energy sector, the *hydrogen economy* is one of the more promising proposed systems. It is based on the fact that the burning of hydrogen gives only water as byproduct, rendering it a very clean technique for energy consumption. Hydrogen can, in principle, be produced by water-splitting. Moreover, it benefits from the fact that biomass is generally very hydrogen-rich, and as such is an energy resource. Importantly, biomass is considered as a *renewable* source due to its reasonable lifecycle timescale. The high hydrogen content of biomass is often related to a wealth of alcoholic functionalities, rendering alcohol acceptorless dehydrogenation (AAD) research fundamental in order to develop efficient techniques for biomass based hydrogen economy. In the Fig. 1.1 below is illustrated the general idea behind the use of renewable resources combined with modern catalytic techniques to yield energy or chemicals for the industry.

Alcohol acceptorless dehydrogenation is the production of hydrogen via hydrogen extrusion from an alcoholic functionality. Accordingly, a carbonyl unit is concomitantly formed, which might be useful for the bulk chemicals industry (see e.g. Fig. 1.2). Preferably, a catalytic system carries out this type of reaction. In general, two main types of catalysis exist: heterogeneous and homogenous catalysis. As the terms imply, heterogeneous catalysis is operating with a catalyst, which is in an different phase than that of the reactants, whereas all is in one phase in homogeneous catalysis. In addition, biocatalysis, catalysis by enzymes, is often regarded as a type of itself, but it is strictly speaking a sublevel of heterogeneous catalysis. All three types of catalysis have been used to address the issue of hydrogen production. However, for simplicity, both heterogeneous and biocatalysis will not be discussed further in this review. Hence, alcohol acceptorless dehydrogenation by homogeneous catalysis is the main topic of this review. In addition, whereas many reviews describe alcohol acceptorless dehydrogenation promoted by heterogeneous

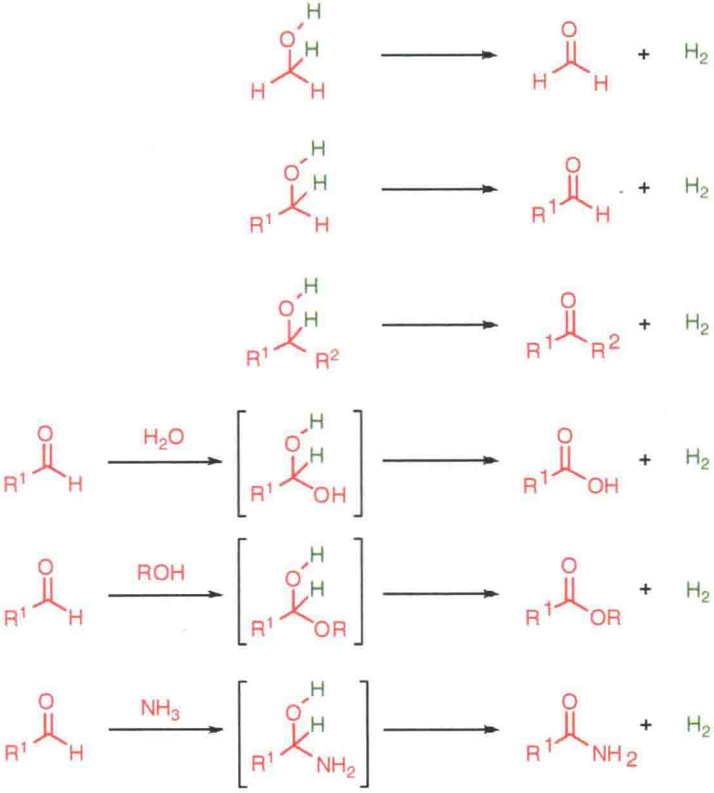


Fig. 1.2 Alcohols to carbonyl units via alcohol acceptorless dehydrogenation (AAD). Examples are given with formaldehyde, aldehydes in general, ketones, acids, esters, and primary amides. R-substituents constitute alkyl and aryl substituents

catalysis methods, very few exist for homogeneous catalysis and none is comprehensive with respect to the topic mentioned here (see e.g. Friedrich and Schneider 2009; Johnson et al. 2010; Dobereiner and Crabtree 2010; Crabtree 2011; Marr 2012; Nova et al. 2010; Walton and Williams 2010). This renders such a report more timely.

## 1.2 Fundamentals of Alcohol Acceptorless Dehydrogenation by Homogeneous Catalysis

The essence of acceptorless dehydrogenation is the oxidation of a substrate with concurrent hydrogen evolution. Hence, a dehydrogenation of an alcohol results in a carbonyl unit and a $H_2$ molecule. Primary alcohols yield aldehydes, and secondary alcohols gives ketones, as shown in Fig. 1.2. Aldehydes can then undergo another round of dehydrogenation to afford, for example, esters or amides.

The oxidation of a C—O single bond to a C═O double bond is thermodynamically unfavorable. Therefore, traditionally, alcohol acceptorless dehydrogenation (AAD) has been accompanied by the reduction of a sacrificial reagent in order to drag the reaction towards full formation of the desired carbonyl product (Fig. 1.3). A typical sacrificial reagent is acetone. In this type of reaction system, the product is called the *Oppenauer product* and the reduced sacrificial reagent the *Meerwein-Ponndorf-Verley (MPV) product*. Because the carbonyl is the desired product, the reaction is termed an *Oppenauer oxidation (OPP)*. However, more generally used terms are *transfer hydrogenation* or *hydrogen borrowing chemistry*.

The overall mechanism of transfer hydrogenation reactions generally involves a delivery of a proton and a hydride from the alcohol to a metal complex, which then transfers them to the MPV reagent, or occurs via a intermediate where both the OPP and MPV reagents are simultaneously coordinated to a metal complex. Consistently, the proton arises from the O*H* unit and the hydride from the C*H* center from the OPP reagent, as shown in Fig. 1.4. Likewise, a hydride coordinated to the metal complex reacts with the carbonyl at the carbon atom, and a proton with the forming alcohol oxygen atom of the MPV reagent.

Two general mechanisms for the hydride transfer between an alcohol and a defined organometallic complex exist. Example **A** in Fig. 1.4 shows the *inner sphere* mechanism, in which a RO-M covalent bond is initially formed via an oxidative insertion of the metal into the O—H bond. This is followed by a *β-hydride elimination*, which leads to the oxidation of the alcohol to the carbonyl and formation of a metal-dihydride (a metal-dihydride is not always the actual resulting complex, but that is beyond the scope of this review). The latter step requires a free site on the metal *cis* to the coordinated alcohol in order to proceed. Nevertheless, there are many examples of AAD reaction steps using a complex with no vacant *cis* sites. In such situation, the other mechanism, *outer sphere dehydrogenation* (Fig. 1.4, Example **B**), is likely to occur. In this mechanism, no prior ligation of the substrate takes place. Instead, a transient pre-coordination via hydrogen bonds between the CH and the metal, and OH and a ligand lone pair donor, facilitates the dehydrogenation. Hence, contrary to the inner sphere mechanism, where both hydrogen atoms are placed on the metal, the outer sphere mechanism utilizes the ligand for the storage of one the hydrogen atoms.

For the reduction of the sacrificial agent, the mechanisms are the same. As such, if a given metal complex dehydrogenates an alcohol through e.g. an outer sphere

**Fig. 1.3** Oppenauer oxidation using acetone as the sacrificial agent. *OPP* = Oppenauer oxidation (product). *MPV* = Meerwein-Ponndorf-Verley (product). Two hydrogen atoms are extruded from the *red-colored* alcohol and given to the *blue-colored* carbonyl substrate (acetone in this example). R-substituents constitute alkyl and aryl substituents

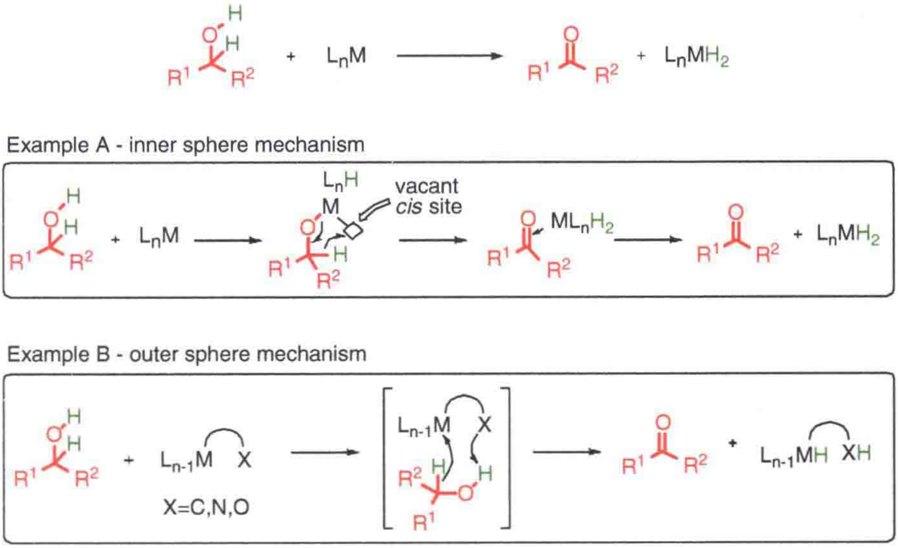
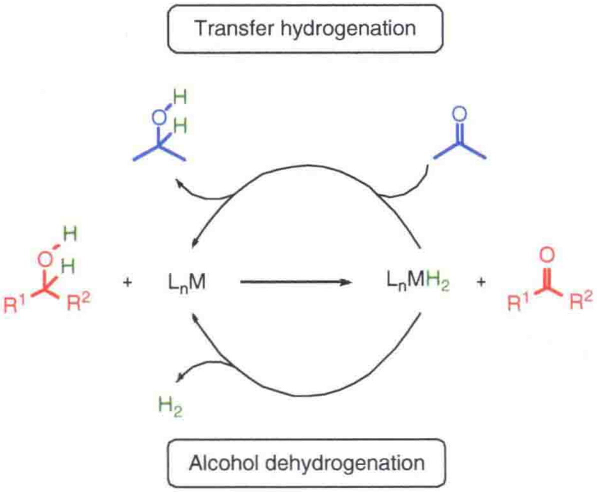


**Fig. 1.4** Alcohol acceptorless dehydrogenation (AAD) by a defined metal complex. In **Example A**, an inner sphere mechanism is shown. Here, a precoordination of the alcohol oxygen atom to the metal (M) occurs. In **Example B**, an outer sphere mechanism is shown. Here, no precoordination occurs. R-substituents constitute alkyl and aryl substituents. $L_n$ constitutes ligands

mechanism, the corresponding hydrogenation of an carbonyl is carried via the same outer sphere mechanism as well. This is the case for transfer hydrogenation; however, for alcohol *acceptorless* dehydrogenation there is no sacrificial agent. For such a system to proceed efficiently, the dihydride metal complex must be sufficiently labile in order to simply release the two hydrogen atoms as a $H_2$ molecule (Fig. 1.5). Because the dihydride metal complexes are usually relatively stable and alcohol oxidation to a carbonyl with no concomitant sacrificial carbonyl reduction is an endergonic process, there is a historical prevalence for the transfer hydrogenation. However, the alcohol acceptorless dehydrogenation process presents a number of important advances, which renders it interesting to develop. The atom economy is much better due to the fact that no sacrificial agent is used. This is also most likely to provide a much easier product purification. A more subtle advantage in this regard is that any possible undesired side reactions between the sacrificial agent (or its MPV product) and the substrate or product is avoided. In addition, along with carbon-based product formation $H_2$ is generated, which is a highly valuable product in itself. As discussed earlier, this can be envisioned to be part of a future energy system based on the hydrogen economy.

Overall, there are four classes of alcohols that are relevant for alcohol acceptorless dehydrogenation reactions with respect to either organic product formation and/or $H_2$ production: model substrates for $H_2$ production, biorelevant substrates for

**Fig. 1.5** Difference between transfer hydrogenation and alcohols acceptorless dehydrogenation (AAD). In transfer hydrogenation (*upper reaction*), a carbonyl substrate takes the hydrogen atoms produced from dehydrogenating the alcohol. In AAD (*lower reaction*), these hydrogen atoms are liberated as $H_2$. R-substituents constitute alkyl and aryl substituents



organic product formation and $H_2$ production, $H_2$ storage relevant alcohols, and substrates with synthetic applications for organic production (Fig. 1.6).

The model substrates constitute a class of alcohols that are themselves not important for $H_2$ production but are very useful for testing new catalytic systems. Each of them represents a simplified substrate compared to biorelevant substrates or complex product precursors. Isopropanol constitutes the simplest model substrate as it is the smallest symmetric secondary alcohol possible, leading to the easily handled acetone when dehydrogenated. This is advantageous for several reasons; Using a secondary alcohol/ketone system allows for a more easy dehydrogenation from a thermodynamic point-of-view. Obtaining a ketone product avoids potential problems related to aldehydes because of the lower reactivity of the former. Thus, less undesired side-reactions and catalyst inactivation are achieved. In addition, the small size of isopropanol circumvent most reactivity issues related to steric clash between substrate and catalyst. In turn, these facts also result in a much easier analytical processing of the reaction mixture.

Moving from isopropanol towards sorbitol, the substrate gradually becomes more complex. $RCH_2CH_2OH$ represents higher alcohols than ethanol, which are useful substrates for testing primary alcohols which are higher boiling than ethanol. This is often necessary due to the high temperature needed for catalyst activity of known catalysts. However, even though this alcohol type is placed in this class, it will often be discussed in the chapter of substrates with synthetic applications because of a generally higher focus on the products in reports of this type. Ethylene glycol and 1,4-butanediol both constitutes diols, which model different situations in biorelevant polyols. Ethylene glycol represents a situation where possible substrate chelation to the catalyst metal might be responsible for catalyst deactivation. In addition, having a hydroxy unit on the α-position to the alcohol to be dehydrogenated inherently changes both its steric and electronic properties. Moreover, polymerization is a possibility/risk. Polymerization is not a concern with 1,4-butanediol where

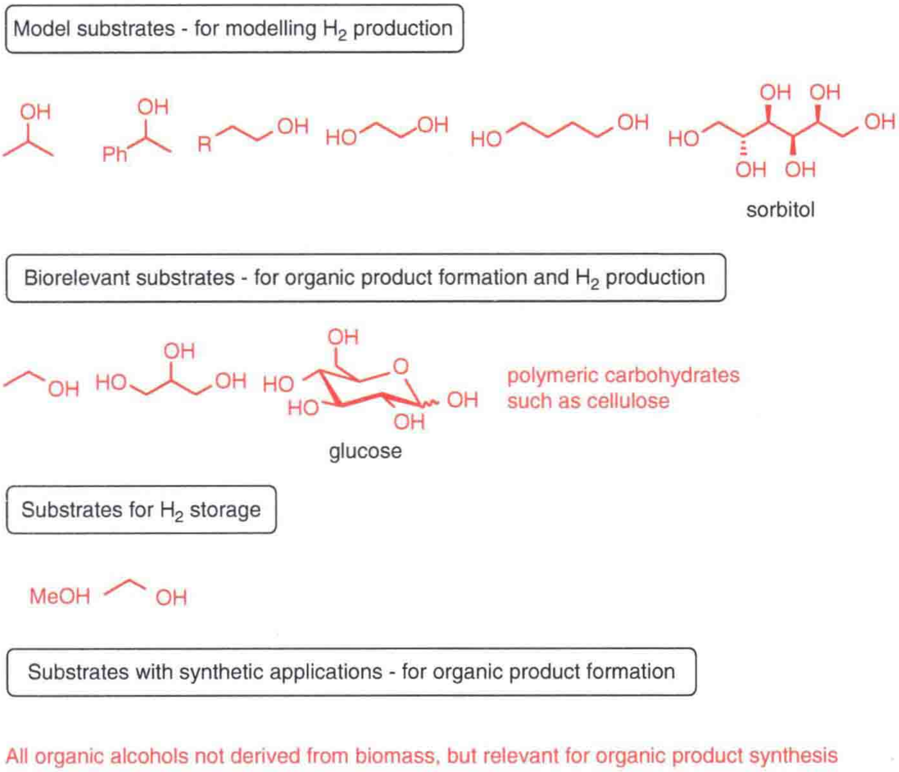


**Fig. 1.6** Classes of relevant alcohols and some examples of each class. The four classes are divided according to biorelevance and application

lactonization is much more favorable. Indeed, this ring-closing feature is the very reason for studying this substrate. Investigation into factors affecting the extent of lactonization may be of importance for further studies with biorelevant polyols.

Moreover, until recently most modern published research has been focusing on these substrates, showing the difficulty in obtaining effective systems with the more complicated biorelevant substrates. It should be mentioned again that some of these model substrates are also represented in the class of substrates with synthetic applications.

The class of biorelevant substrates includes alcohols that can be extracted from biomass in considerable amounts and used for organic product formation and/or $H_2$ production. The best scenario is, of course, that the organic product left after $H_2$ formation is a useful material for the chemical industry. The simplest alcohol of this class is ethanol, which is termed bioethanol if it originates from biomass. In order to be of interest from an energy production point-of-view, bioethanol should be available without the need for severe purification processes, such as numerous distillations. This complicates the catalytic system since especially water may be a severe impurity.