



Review

Potential effect of ultrasound on carbohydrates

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ABSTRACT

The use of ultrasound has emerged as one of the most useful alternative energy sources for the synthesis of carbohydrate-derived biologically and pharmaceutically potential compounds. Spectacular advances have been made in the field of sonication-assisted organic reactions, which are known for producing superior yields, enhanced reactivity of the reactant, improved stereoselectivity, and shortened reaction times. Orthogonal protection-deprotection reactions and/or modification and manipulation of functional groups in carbohydrates are common synthetic steps in carbohydrate chemistry. These reaction steps can be driven by the ultrasonic energy generated by acoustic cavitation via the formation and subsequent collapse of ultrasound-induced bubbles. The ultrasound-assisted synthesis of differently functionalised monosaccharides is useful in a wide variety of applications of carbohydrate chemistry such as the glycosylation of oligosaccharides, one pot domino reactions, thioglycoside syntheses, azidoglycoside syntheses, 1,3-dipolar cycloaddition reactions, and syntheses of natural products. This review article covers ultrasound-mediated reactions on carbohydrates that have been described in the literature since 2000.

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1. Introduction

Carbohydrates are essential components in all forms of life and are crucial for biological recognition processes. For example, the carbohydrates on the cell surface can serve as receptors for other cells, pathogens, toxins, and other molecules. They are also implicated in the development of several diseases, such as an aberrant glycosylation in the cell membranes of tumor cells.^{1a} As a consequence, carbohydrates have been the focus of a significant amount of research both in biology and chemistry, including their synthesis and a mechanistic understanding of their role in metabolic pathways. Due to their structural diversity and ability to form inter- and intracellular bridges, these biomolecules are more than just an essential part of the structural framework of cells and tissues. In addition, oligosaccharides, glycoproteins, glycolipids and other glycoconjugates are often the key elements in signalling processes, cell-cell communication, pathogen defense, and molecular and cellular targeting.^{1b}

Carbohydrate-based materials are also being used for the development of new classes of therapeutic agents, including

anticoagulants such as low molecular weight heparins and fondaparinux; α -glycosidase inhibitors for diabetes treatment such as voglibose, miglitol, and acarbose; and viral neuraminidase inhibitors such as zanamivir and oseltamivir.² Monosaccharides in particular can be used as chiral pools for the asymmetric synthesis of natural products and pharmaceutically active ingredients (Fig. 1).³ On the other hand, the structural complexity of larger, densely functionalized carbohydrates such as oligosaccharides and polysaccharides render their chemical syntheses difficult. The biggest challenges in carbohydrate synthesis are not only the stereoselective glycosylation of two or more sugars but also the construction of orthogonally protected monosaccharide derivatives.⁴ In the case of protecting group manipulation, it is essential to prepare regioselectively protected saccharides so that other functional groups can be introduced at their desired positions.⁵ Orthogonal protection-deprotection and the control of chemistry at the anomeric centre of monosaccharides is very challenging in carbohydrate chemistry, particularly during the synthesis of carbohydrate building blocks or glycosyl 'donors' and 'acceptors' for glycosylation reactions.^{6,7}

The synthesis of carbohydrate biomolecules from carbohydrate materials or the carbohydrate-based Chiron approach for the synthesis of natural products, active pharmaceutical ingredients (API) and building blocks for clinical, industrial and academically

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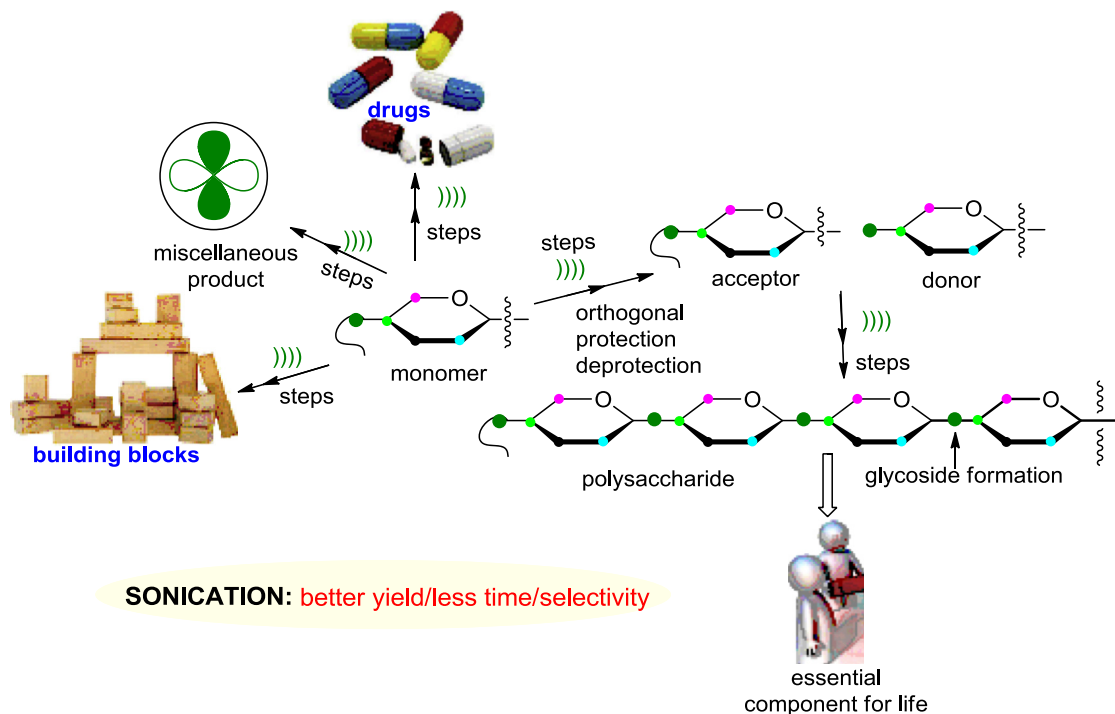


Fig. 1. Use of sonication in carbohydrate chemistry.

potential compounds are not new to chemists. The novelty is the development of environmentally benign approaches in their chemical synthesis that could address several future challenges, in working with chemical processes and in the quality and quantity of the products by inventing greener reactions. Green approaches may have the potential to enhance yields of desired products, to minimize time and by-products, and to simplify operations in chemical production by using environmentally and ecologically benign, nontoxic, less hazardous, and less carcinogenic non-volatile solvents.^{8,9} Ultrasound energy is one of several environmentally friendly sources of energy for chemical reactions, and can lead to high efficiency, low waste, low energy requirements, and enhancement of reaction rates by many orders of magnitude.^{10–18}

The first use of ultrasound (100–500 KHz) was effected by A. L. Loomis in 1927¹⁹ for the hydrolysis of dimethyl sulfate and the iodine clock reaction. Since then, it has been used to accelerate reaction rates in a wide variety of chemical reactions, resulting in a sub-discipline called 'sonochemistry'. In addition to the sonochemical reaction, ultrasound energy is also used for homogenization (dispersing and de-agglomeration, emulsifying wet-milling and grinding), disintegration (cell extraction and hot water disinfection), welding of thermoplastics, degradation of performed plastics, degassing or cleaning of unwanted materials, medical imaging (2–10 MHz), physiotherapy, dentistry, and sound navigation and ranging (SONAR) technique in ship navigation. Generally, sonochemistry operates in the region of 20 KHz to 1 MHz. Therefore, this technology is characterized by high energies that disperse the reagents and that also initiate as well as accelerate the reactions. This ultrasound-mediated chemistry is governed by different parameters that include the amplitude and frequency of the applied sound field, temperature, surface tension, vapour pressure, gas content and nuclei density of the solution, and vessel and probe geometry. However, sonochemical reactions are not affected by acidity, basicity, or dipole moment. Ultrasound waves having low energies (20 KHz–500 MHz) are not capable of directly

altering electronic, vibrational, or rotational molecular states, but indirectly affect chemical reactions, via the cavitation phenomenon, which results in enough energy to alter vibrational and rotational molecular states. The formation of acoustic cavitations of micro-bubbles, which grow and collapse continuously, results in the generation of temperatures of 5000–8000 K and pressures greater than 10,000 atm on a nanosecond timescale within the vapour phase of the bubble, followed by cooling at a rate as fast as 10^9 K/s (Fig. 2).²⁰ Due to this local heating combined with extraordinarily rapid cooling, this method provides a unique means for driving significant gas phase chemical reactions, which are important in a variety of applications. The following sonochemical effects can be observed in chemical reactions and processes: an increase in rate and yield of the reaction, increased reactivity of reagents or catalysts, switching of the reaction pathway, activity improvement of phase transfer catalysts, avoidance of phase transfer catalysts, activation of metals and solids, improvement of particle and

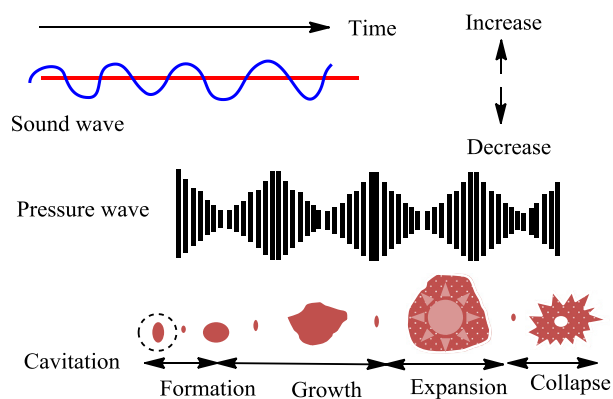


Fig. 2. Mechanistic pathway for the generation of energy in sonication.

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