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Halogenase Enzymes for Synthesis Development

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Abstract

Nature has evolved halogenase enzymes that halogenate a wide range of biosynthetic precursors regioselectively, with the halogens added often having a significant impact on the biological activity of the ensuing natural products. Synthetic aims to develop non-natural bioactive small compounds for medicinal and cosmetic applications. A similar finding has been reached in agrochemical applications. Halogens can significantly improve the characteristics of organic compounds, allowing them to modulate biological targets selectively in vivo. As a result, halogens are found in a large number of medications and agrochemicals on the market today. Halogenated organic molecules are also popular synthesis intermediates, and they're especially useful in cross-coupling reactions involving metal catalysts.

Introduction

Traditional nonenzymatic halogenation chemistry, despite the potential value of organohalogens, uses harmful chemicals and frequently lacks regiocontrol. In order to produce cost-effective and environmentally acceptable industrial processes, reliable, simple, and cleaner methods for regioselective halogenation of organic molecules are required. The utilisation of halogenase enzymes, which are responsible for the biosynthesis of halogenated natural compounds, as biocatalysts could be one route to such techniques.The progress in producing halogenases for biocatalysis, as well as potential untapped sources of such biocatalysts, will be discussed in this review, as well as how additional optimization of these enzymes is required to attain the aim of industrial scale biohalogenation. Many pharmaceutical and agricultural products, as well as other useful materials, contain organohalogen moieties, which are widely employed in all sectors of the chemical industry in the form of synthetic intermediates. Because of the numerous C-C, C-F, C-N, and other C-heteroatom couplings that are possible, transition metal-catalyzed crosscoupling processes have become crucial tools for the synthesis of complex compounds possible. Because of their capacity to metalate C-X bonds, organohalogens are used in many of these reactions, and halogenated compounds are now common intermediates in organic synthesis. Furthermore, the addition of a halogen atom to a tiny molecule can have a significant impact on its bioactivity and physical properties. This property has been utilised in medicinal chemistry, with halogen atoms found in a substantial fraction of all medications in clinical trials or on the market. It has been proven that the halogen substituents are critical for antibacterial action in the antibiotic vancomycin, with dechlorovancomycin variants demonstrating considerably lower binding affinity for the biological target peptidoglycan. The halogen's unique effect on biological activity has extended to the design of agrochemicals, with many of the most popular herbicides, pesticides, and insecticides including halogen. Organohalogen compounds have also been discovered to have desirable characteristics in

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polymers, and as a result, they are garnering more consideration for future material generations. The effect of halogens on bioactivity and bioavailability was previously assumed to be mainly attributable to lipophilicity modulation and nonspecific hydrophobic interactions with protein targets. Carbonhalogen bonds, on the other hand, have recently been found to generate directed intermolecular interactions with proteins, known as halogen bonds. These are caused by the halogen's electron-deficient "sigma-hole" in a CX bond, which allows halogens to interact with lone pairs of heteroatoms like N, O, and S in protein targets in a way similar to hydrogen bonding. As a result, using halogen atoms in medicinal chemistry is a well-established practise since it allows for the introduction of additional ligandtarget interactions without requiring significant changes to other interactions with the target.