

SYNTHESIS AND INVESTIGATION OF OXIDIZING REAGENTS BASED ON 2-IODOBENZENESULFONIC ACID

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For the last 5 years, 6939 articles with the keyword “hypervalent iodine” were published in editions that are peer-reviewed by international databases such as Scopus and Web of Science. Hypervalent iodine compounds have reactivity, which is similar to transition metals, and, therefore, they have ecologically benign nature [1]. These compounds are widely used in organic synthesis as effective selective reagents for oxidation and functionalization of various organic substrates. So, for instance, hypervalent iodine reagents are utilized in reactions of C–C, C–N, C–S, C–F-bond formation, in important oxidizing transformations, rearrangements, an also in reactions that are catalyzed by transition metals [1–3, 4]. Existing reagents based on hypervalent iodine such as IBX (2-iodoxybenzoic acid) and DMP (Dess-Martin Periodinane) have limited application and require special reaction conditions. Consequently, a design of new oxidizing reagents that have high reactivity and selectivity and as well as correspond to “green” chemistry principles is highly relevant [1–2, 5].

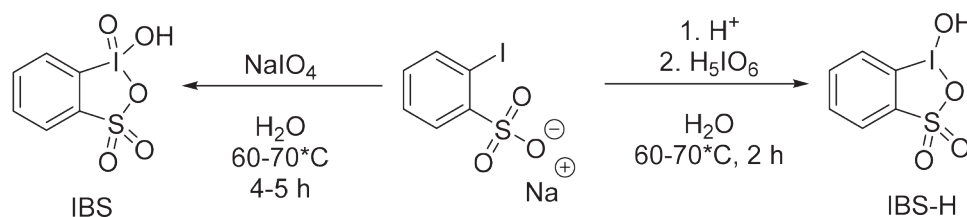
2-Iodoxybenzenesulfonic acid (IBS) is a thia-analogue of 2-iodoxybenzoic acid. IBS exhibits stronger oxidation properties than the precursor due to the strong electron-withdrawing sulfo-group in its composition. Earlier the preparation of IBS

was obstructed because of high solubility in water as well as the oxidant that is used for IBS preparation and, furthermore, IBS has high reactivity toward organic solvents. We carried out an optimization of obtaining of 2-iodoxybenzenesulfonic acid with the use of different oxidants (Scheme 1). It let to extract IBS in individual form and X-Ray analysis was conducted.

Firstly, oxidation was conducted with periodic acid but sodium 2-iodobenzenesulfonic acid was converted to acidic form by ion exchange with help of Amberlyst 15 (H⁺). The oxidation of 2-iodobenzenesulfonic acid proceeds with the formation of hypervalent iodine (III) compound – 2-iodosylbenzenesulfonic acid (IBS-H) (Scheme 1). This suppose was proved by ¹H and ¹³C NMR spectroscopy.

Secondly, the oxidation with a utilization of sodium periodate was conducted in the same conditions but for the full conversion of the substrate the reaction time was increased. As a result, 2-iodoxybenzenesulfonic acid (IBS) was obtained.

The prepared reagents were investigated in oxidation reactions of various organic compounds. It was found that they were able to oxidize hydroxyl-containing substrates to carbonyl substances but it should be noted IBS-H is less active than IBS in these reactions.



Scheme 1. Preparation of 2-iodoxybenzenesulfonic acid and 2-iodosylbenzenesulfonic acid from sodium 2-iodobenzenesulfonate

References

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