

SYNLETT Spotlight 182

Sodium Periodate (NaIO_4) – A Versatile Reagent in Organic Synthesis

Compiled by Majid Rezaeivalla

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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Introduction

Sodium periodate (sodium metaperiodate), NaIO_4 (mp 300 °C; Figure 1), is commercially available and is applied mainly in aqueous or aqueous–alcoholic solutions. Like the free periodic acid, sodium periodate cleaves vicinal diols to carbonyl compounds.¹ The popularity stems from its specificity, its reactivity under neutral and mild conditions which is compatible with a wide range of functionalities, its stability, and its low cost.² Sulfides are transformed by sodium periodate into sulfoxides. It is also a reoxidant of lower-valency ruthenium in oxidations with ruthenium tetroxide.³

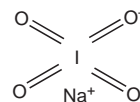
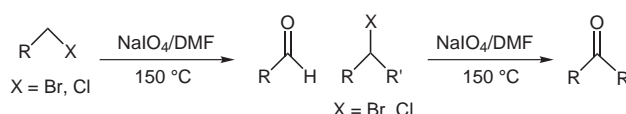


Figure 1

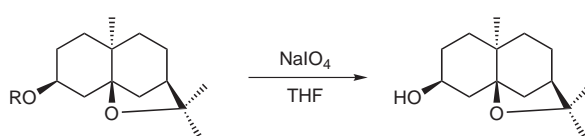
Tetrabutylammonium periodate, $(n\text{-Bu})_4\text{NIO}_4$ (mp 175 °C), which is usually prepared in situ from tetrabutylammonium hydrogen sulfate and sodium periodate,⁴ is useful in two-phase systems, because it dissolves in chloroform and other organic solvents.³ It is used in homogeneous oxidations of sulfides, 2-hydroxy acids, and α -bromoketones.⁵

Abstracts

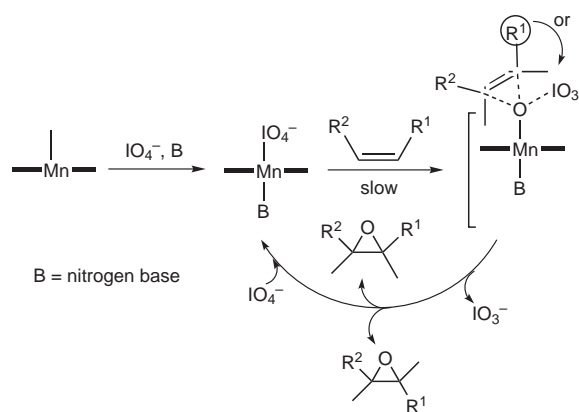
(A) NaIO_4 /DMF oxidizes various primary and secondary halides to the corresponding aldehydes and ketones under mild conditions (150 °C, 40–60 min) in high yields (70–90%).⁶



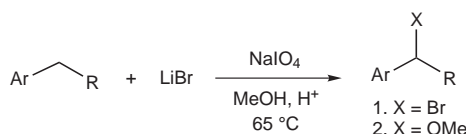
(B) A mild and efficient method for the deprotection of silyl ethers is reported. The most often used silyl protecting groups, such as TBDMS, TIPS, TMS, TES, TIBS, and TPS can be cleaved by NaIO_4 furnishing the corresponding alcohol in high yield. This method can be used for a wide range of substrates.⁷



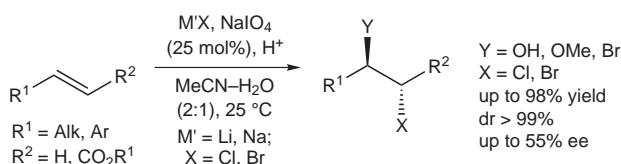
(C) A highly stereoselective epoxidation (>95%) of unfunctionalized alkenes was performed by tetrabutylammonium periodate in the presence of six different phenyl-substituted manganese(III) *meso*-tetraphenylporphyrins [Mn(Por)] and imidazole in CH₂Cl₂.⁸



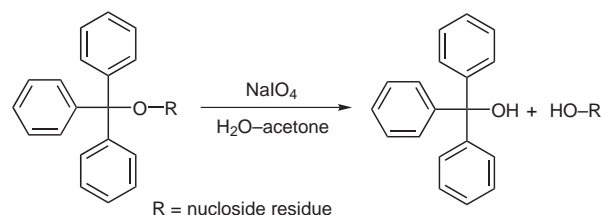
(D) Sodium periodate mediates the C–H activation of alkylbenzenes and alkanes with LiBr efficiently under acidic conditions, producing the corresponding bromo and acetoxy derivatives in excellent yields.⁹



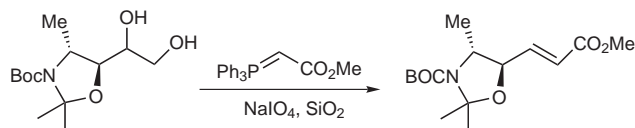
(E) NaIO₄ oxidizes alkali metal halides efficiently in aqueous medium to halogenate alkenes and aromatics and produce the corresponding halo derivatives in excellent regio- and stereoselectivity. The system also demonstrates the asymmetric version of bromo hydroxylation using α -cyclodextrin complexes, resulting in moderate ee values.¹⁰



(F) Cleavage of the *O*-(dimethoxytrityl) group using neutral sodium periodate is reported.¹¹ Sodium periodate in aqueous organic solvents selectively removes the *O*-(dimethoxytrityl) protecting group under mild reaction conditions. The selectivity of the cleavage was studied using the nucleoside derivatives protected by various types of groups commonly used in nucleoside and nucleotide chemistry.¹¹



(G) Oxidative cleavage of a series of glycols using NaIO₄ on silica gel in the presence of a series of stabilized ylides provides access to a number of synthetically useful alkenes. The ease and general utility of this reaction is demonstrated here using several carbohydrylates and amino acids.¹²



References

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