

SYNLETT Spotlight 361

Sodium Dithionite

Compiled by Xiao-Nan Zhang

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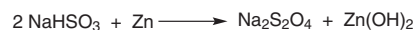
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Introduction

Sodium dithionite (also known as sodium hydrosulfite) is a versatile, inexpensive, safe and readily available reagent, which has been employed for more than 70 years. It has been used in biochemistry for the reduction of a variety of coenzymes and enzymes, and in organic synthesis to reduce several types of functional groups, such as aldehydes, ketones, imines, pyrazine, vinyl sulfones, nitro¹ and azo groups,² oximes,³ enones,⁴ quinones,⁵ and azides.⁶ It was also found to be an efficient reagent for the reductive displacement of iodine⁷ and reductive coupling of benzylic and allylic halides.⁸ It has been also used as radical initiator to promote coupling of CF₃CHClBr with 1,3,5-trimethoxybenzene,⁹ the addition of 1-bromo-1-chloro-2,2,2-trifluoroethane to the terminal double bond of

allylbenzenes,¹⁰ addition reaction of perfluoroalkyl iodides with allenes,¹¹ the reaction of polyfluoroalkyl iodides with alkenes,¹² addition of dialkyl phosphonodifluoromethyl radical onto unsaturated ketones,¹³ fluoroalkylation of porphyrins¹⁴ and vinyl ethers.¹⁵ This reagent is found to be a useful reagent in the intramolecular Marschall cyclization¹⁶ and Claisen rearrangement.¹⁷

Sodium dithionite is now commercially available, but can also be prepared readily by the reaction of sodium bisulfite with zinc.¹⁸ It is obtained as a white crystalline powder with a weak sulfurous odor. This compound is stable under most conditions, but it will decompose in hot water and in acid solutions.



Scheme 1

Abstracts

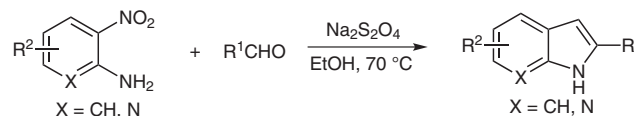
(A) Reduction of Quinones to Hydroquinones:

Suzuki and co-workers showed that 2,5-dihalobenzoquinones could be reduced to the corresponding hydroquinones with aqueous sodium dithionite in high yield.¹⁹



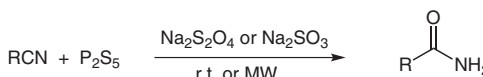
(B) One-Pot Synthesis of Benzimidazoles via Reductive Cyclization:

A highly efficient procedure for the preparation of benzimidazoles in one step by the reduction of *o*-nitroanilines with sodium dithionite in the presence of aldehydes in ethanol is achieved.²⁰ Only monosubstituted benzimidazole was obtained in this procedure. Furthermore, this method was applied to the synthesis of imidazole-containing heterocyclic ring systems.



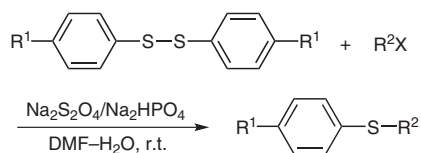
(C) Thioamides from Nitriles and Phosphorus Pentasulfide:

Goswami and co-workers reported that aliphatic, aromatic, and heterocyclic nitriles can be thionated to give the corresponding primary thioamides using a reagent system of phosphorus pentasulfide and sodium dithionite or sodium sulfite.²¹ The thionating nucleophile PS₃⁻ is probably generated by reducing the weak P=S or reductively cleaving the P-S bond of P₄S₁₀ using this reagent system. It attacks the electrophilic carbon of the cyano group to afford thioamide after aqueous work-up.

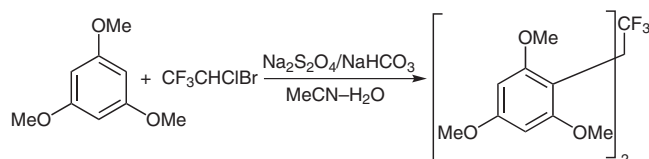


(D) *One-Pot Synthesis of Sulfides by Reaction of Aryl Disulfides with Alkyl Halides:*

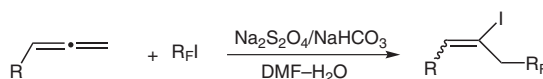
A mild method for the synthesis of unsymmetrical sulfides by reaction of diaryl disulfides with alkyl halides has been developed. Sodium dithionite is speculated to form a radical anion and serves as a source of electrons for the cleavage of the S–S bond or for the dehalogenation of alkyl halides.²²

(E) *Fluoroalkylation of 1,3,5-Trimethoxybenzene:*

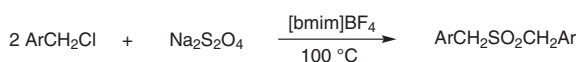
Sodium dithionite can be applied as a radical initiating reagent for fluoroalkylation of 1,3,5-trimethoxybenzene with CF_3CHClBr in acetonitrile–water to afford trifluoromethylbis(2,4,6-trimethoxyphenyl)methane as the only isolated product.²³

(F) *Regio- and Stereoselective Addition of Perfluoroalkyl Iodides to Allenes:*

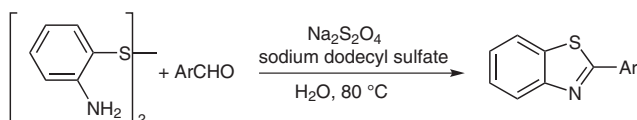
Sodium dithionite has successfully been used as initiator for the selective addition of perfluoroalkyl iodides to various allenes conjugated with a C=O or a P=O double bond. Perfluoroalkyl groups were introduced into the terminal position of allenes regioselectively and adducts with the *E*-configuration were obtained stereoselectively.²⁴

(G) *Synthesis of Symmetric Dibenzyl Sulfones:*

Li et al. have reported a one-step synthesis of symmetric dibenzyl sulfones by reaction of sodium dithionite with benzyl chloride in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{bmim}][\text{BF}_4]$).²⁵

(H) *Synthesis of 2-Arylbenzothiazoles:*

Chen and co-workers showed that sodium dithionite can promote the synthesis of 2-arylbenzothiazoles by reaction of 2,2'-disulfanediyldianiline with aldehydes in the presence of sodium dodecyl sulfate in water.²⁶



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