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Spotlight 361

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

Sodium Dithionite

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Introduction

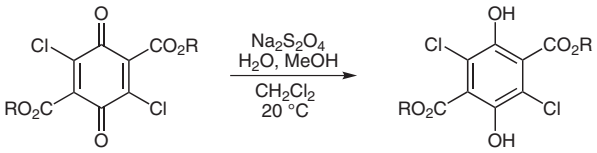
Sodium dithionite (also known as sodium hydrosulfite) is a versatile, inexpensive, safe and readily available reagent, which has been employed for more than 70 years. It has been used in biochemistry for the reduction of a variety of coenzymes and enzymes, and in organic synthesis to reduce several types of functional groups, such as aldehydes, ketones, imines, pyrazine, vinyl sulfones, nitro[1] 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 iodine[7] and reductive coupling of benzylic and allylic halides.[8] It has been also used as radical initiator to promote coupling of $CF_3CHClBr$ with 1,3,5-trimethoxybenzene,[9] the addition of 1-bromo-1-chloro-2,2,2-triuoroethane to the terminal double bond of allylbenzenes,[10] addition reaction of peruoroalkyl iodides with allenes,[11] the reaction of polyfluoroalkyl iodides with alkenes,[12] addition of dialkyl phosphonodifluoromethyl radical onto unsaturated ketones,[13] fluoroalkylation of porphyrins[14] and vinyl ethers.[15] This reagent is found to be a useful reagent in the intramolecular Marschalk cyclization[16] 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.

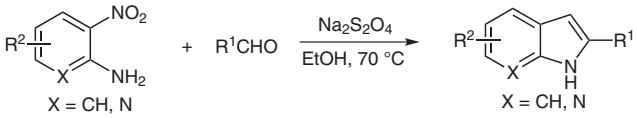
Scheme 1

Abstracts

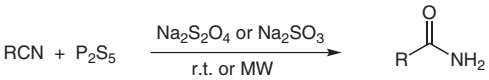
(A) *Reduction of Quininones to Hydroquinones:*
Suzuki and co-workers showed that 2,5-dihalobenzoquinones could be reduced to the corresponding hydroquinones with aqueous sodium dithionite in high yield.[19]



(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 PS_3^- is probably generated by reducing the weak P=S or reductively cleaving the P–S bond of P_4S_{10} using this reagent system. It attacks the electrophilic carbon of the cyano group to afford thioamide after aqueous work-up.



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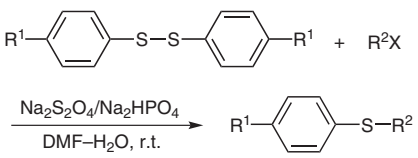
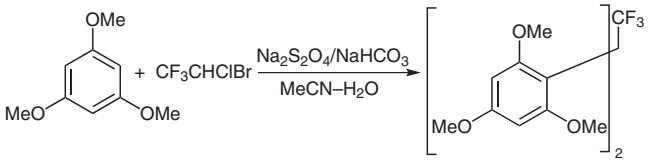
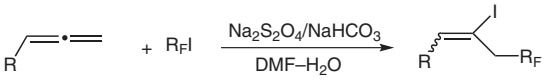
(D) *One-Pot Synthesis of Sulfides by Reaction of Aryl Disulfides with Alkyl Halides*:
A mild method for the synthesis of unsymmetrical sulfides by reaction of diaryl disulfides with alkyl halides has been developed. Sodium dithionite is speculated to form a radical anion and serves as a source of electrons for the cleavage of the S–S bond or for the dehalogenation of alkyl halides.[22]



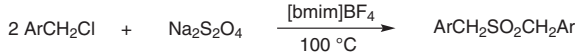
(E) *Fluoroalkylation of 1,3,5-Trimethoxybenzene:*
Sodium dithionite can be applied as a radical initiating reagent for fluoroalkylation of 1,3,5-trimethoxybenzene with $CF_3CHClBr$ in acetonitrile–water to afford trifluoromethylbis(2,4,6-trimethoxyphenyl)methane as the only isolated product.[23]



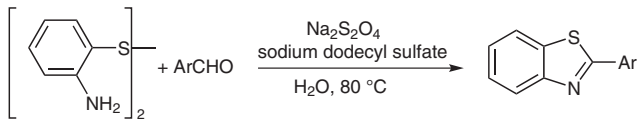
(F) *Regio- and Stereoselective Addition of Perfluoroalkyl Iodides to Allenes*:
Sodium dithionite has successfully been used as initiator for the selective addition of perfluoroalkyl iodides to various allenes conjugated with a C=O or a P=O double bond. Perfluoroalkyl groups were introduced into the terminal position of allenes regioselectively and adducts with the *E*-configuration were obtained stereselectively.[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-methylimmidazolium tetrafluoroborate ([bmim]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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