Sodium Sulfide

Compiled by Fei-Ping Ma

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Introduction

Sodium sulfide is pink to yellowish solid with a rotten egg-like odor. It is readily soluble in water, slightly soluble in alcohol and insoluble in ether. Anhydrous sodium sulfide can ignite spontaneously when exposed to air. It is used in chemical manufacturing as a sulfonation and sulfoxidation agent. It is used in the production of rubber chemicals, sulfur dyes, and other chemical compounds. It has also been used as a reducer for the reduction of nitro compounds to the corresponding amines. It was found to be useful for the conversion of carboxylic acids into thioacids and alkenoyl ketene dithioacetals into the corresponding [5+1]-annulation products as well as for the synthesis of thiophuranose, cyclic dithiocarbonates, tetrahydrothiophene derivatives, 4-bromo-2-nitrobenzenethiol, a-lipoic acid, thieno[2,3-c]pyrazoles, unsaturated thiacyclic ethers, thieno[3,2-c]cinnoline, monomeric cyclic diketosulfides, thiophenes, 4H-thiopyran compounds, 4H-thiocromen-4-ones and benzo[b]thiophenes. It can also act as an atom-economical inorganic nucleophile in transition-metal-catalyzed allylation substitutions.

Sodium sulfide is commercially available and it can be readily prepared by reduction of Na2SO4 with carbon or through a solid–gas reaction of a sulfidizing gas mixture of COS, CS2, and S2 with the reactant of Na2CO3.

Abstracts

(A) Thionation of Carbonyl Compounds:
Salama and co-workers have found that a combination of tetrachlorosilane and sodium sulfide in acetonitrile is an efficient thionating reagent for aromatic aldehydes to afford the corresponding thioaldehydes as trimers in good yields in the absence of catalysis. Under these mild conditions α,β-unsaturated ketones reacted with SiCl4/Na2S in the presence of a catalytic amount of CoCl2·6H2O to give the respective disulfides via β-mercapto ketones.

(B) Regioselective Ring Opening of Epoxides:
Na2S can be applied as a mild sulfur nucleophile for regioselective ring opening of epoxides to give the corresponding bis[β-hydroxyalkyl]sulfides in the presence of poly[N-(2-aminoethyl)acrylamido]trimethyl ammonium chloride resin as a phase-transfer catalyst. The reaction of 2,2-bis(trifluoromethyl)oxiranes with aqueous solution of Na2S leads to the formation of Si(CH2CF3)2OH.

(C) Divinylsulfides:
A convenient and practical method for the direct synthesis of bis(arylviny1) sulfides by the addition of sodium sulfide to arylacetylenes has been developed. These sulfides can be converted chemoselectively into the sulfoxides and sulfones.

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(D) 2-Trifluoromethyl Benzothiophenes:
Li et al. reported a practical protocol for the selective synthesis of 2-trifluoromethyl benzothiophenes by copper-catalyzed thiolation annulation reaction of 1,4-dihalides with Na2S. This protocol allows the formation of two C–S bonds in a one pot reaction through the thiolation annulation of various 1,4-dihalides, including less active dichlorides.25

(E) Substituted 2,3,6,7-Tetrahydrothiopyrano[2,3-b]thiopyran-4,5-diones:
Pan et al. reported a one-pot approach for the synthesis of dissubstituted bicyclic thia-heterocycles via formal double [5+1] annulation of dialkenoylketene dithioacetals using sodium sulfide nonahydrate in DMF.26

(F) Symmetrical Alkyl Disulfides:
A mild and practical method for the synthesis of symmetrical alkyl disulfides from alkyl halides and a mixture of Na2S with sulfur using didecyldimethylammonium bromide (DDAB) as a phase-transfer catalyst has been developed.27 The reactivity order was found to be: didecyldimethylammonium bromide (DDAB) as a phase-transfer catalyst has been developed.27 The reactivity order was found to be: benzyl halide > primary alkyl halide > secondary alkyl halide > tertiary alkyl halide > aryl halide.

(G) Angular Anthrathiophenediones:
In addition to the above cases, the cyclocondensation of available vic-alkynylchloroanthraquinones with Na2S is a convenient method for the synthesis of angular anthrathiophenediones.28

References

(4) Pan, L.; Liu, Q. Synlett 2011, 1073.