

SYNLETT Spotlight 378

Rongalite

Compiled by Jiu-Xi Chen

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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

Rongalite (also known as sodium formaldehyde sulfoxylate or sodium hydroxymethanesulfinate) is a versatile, inexpensive and readily available reagent, which has been employed twenty years ago.¹ It is commonly used in the textile industry as a decolorizing agent. Several reports are available in the literature demonstrating its utility in organic synthesis. For example, rongalite is capable of producing the perfluoroalkyl free radicals via dehalogenation of alkyl halides,^{2–4} such as direct perfluoroalkylation of pyridines,⁵ coumarins⁶ and 2-quinolones.⁷ It has been also used for the cleavage of diaryl disulfides and dis-

lenides generating the corresponding chalcogenolate species in situ that then undergo facile ring opening and acylation, affording β -hydroxy sulfides,⁸ thioesters and selenoesters,⁹ respectively. It was also found to be a sulfoxylate dianion equivalent in the conversion of dihalides into sultine derivatives.^{10–15}

Rongalite is commercially available, but it can also be readily prepared by reaction of formaldehyde with sodium sulfite.¹⁶

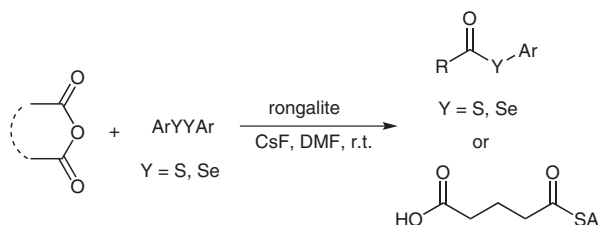


Scheme 1

Abstracts

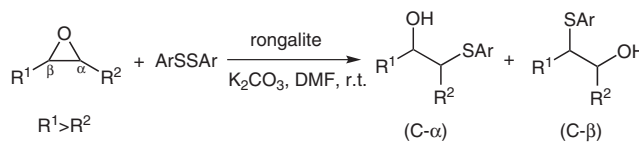
(A) One-Pot Synthesis of Thioesters and Selenoester via Reaction of Diaryl Disulfides with Anhydrides:

A simple, efficient and broadly applicable general method for the synthesis of thioesters in one step by acylation of diaryl disulfides with aromatic, aliphatic or cyclic anhydrides in the presence of rongalite and CsF has been developed. Furthermore, this method was applied to the synthesis of seleno esters. Rongalite is speculated to promote cleavage of diaryl disulfides generating chalcogenolate anions that then undergo facile acylation with anhydrides in the presence of CsF to afford the corresponding thioesters and selenoesters.¹⁷



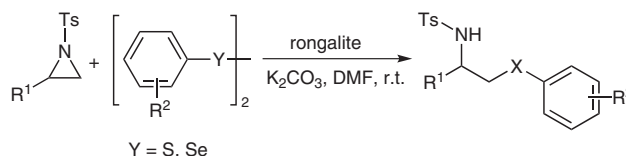
(B) Highly Regioselective Ring Opening of Epoxides with Diaryl Disulfides for the Synthesis of β -Hydroxy Sulfides:

Rongalite has successfully been used as initiator for the highly regioselective ring opening of epoxides with diaryl disulfides to the corresponding α -addition products in good to excellent yields.^{18–19} It should be noted that the thiolate anion attacks the epoxides derived from styrene to produce the corresponding α -addition products with high regioselectivity, instead of the β -addition regioisomer that could be formed from the attack of the nucleophile at the benzylic position.

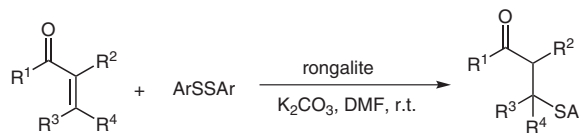


(C) One-Pot Synthesis of β -Amino Sulfides and Selenides:

The same year, Chandrasekaran and co-worker reported that reductive cleavage of diaryl disulfides and diselenides mediated by rongalite followed by ring opening of aziridines provides easy access to β -amino sulfides and β -amino selenides in a stereospecific and regioselective manner under mild conditions in a one-pot operation.¹⁹

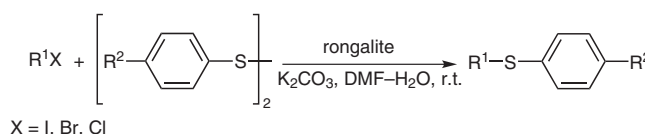
(D) Synthesis of β -Sulfido Carbonyls by Thia-Michael Addition of Diaryl Disulfides to α,β -Unsaturated Ketones and Esters:

The above reducing system has also been applied for the thia-Michael addition of diaryl disulfides to α,β -unsaturated ketones and esters, affording the corresponding β -sulfido carbonyl compounds with high chemoselectivity in good to excellent yields.²⁰ A plausible mechanism for the role of rongalite, as initiator for the cleavage of disulfides generating thiolate anions that then undergo facile thia-Michael addition to α,β -unsaturated ketones and esters is proposed.



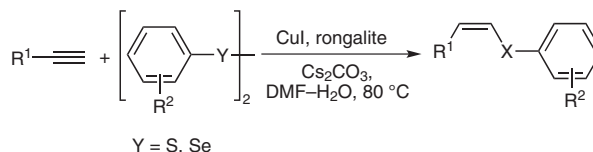
(E) One-Pot Synthesis of Sulfides by Reaction of Aryl Disulfides with Alkyl Halides:

Zhong and co-workers reported that a one-pot, efficient synthetic method for the preparation of unsymmetrical sulfides by the treatment of diaryl disulfide with alkyl halides in the presence of rongalite has been developed. Two possible reaction pathways for the formation of unsymmetrical sulfides are discussed.²¹



(F) Hydrothiolation of Terminal Alkynes with Diaryl Disulfides and Diphenyl Diselenide:

In the presence of CuI, rongalite, and Cs_2CO_3 , a variety of disulfides underwent stereoselectively the hydrothiolation of terminal alkynes with diaryl disulfides, achieving the corresponding (*Z*)-1-alkenyl sulfides in moderate to excellent yields. The reaction has been extended further to hydroselenations of 1,2-diphenyldiselenane with alkynes in a stereoselective manner for the synthesis of (*Z*)-1-alkenyl selenides in good yields.²²



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