

S8: A cheap and sincere reagent

Compiled by Javad Afsar

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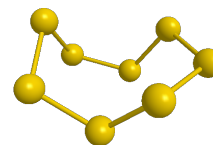
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

Sulfur (S) with atomic weight 32.064 and atomic number 16, have four naturally isotopes [32 (95.0%), 33 (0.76%), 34 (4.22%), 36 (0.014%)] and artificial, radioactive isotopes (29-31, 35, 37, 38). Exist both the free-state and in combination, as sulfides and sulfates at crust of the earth and has been known from ancient times. Sulfur industrial prepared by Frasch process [1]. Among elements, sulfur has the most solid allotropes (about 30 well characterized allotropes). Most of them are in cyclic form with ring sizes range from 6 to 20 and depending on the conditions during preparation, divided in two groups: high-pressure allotropes and ambient pressure allotropes.

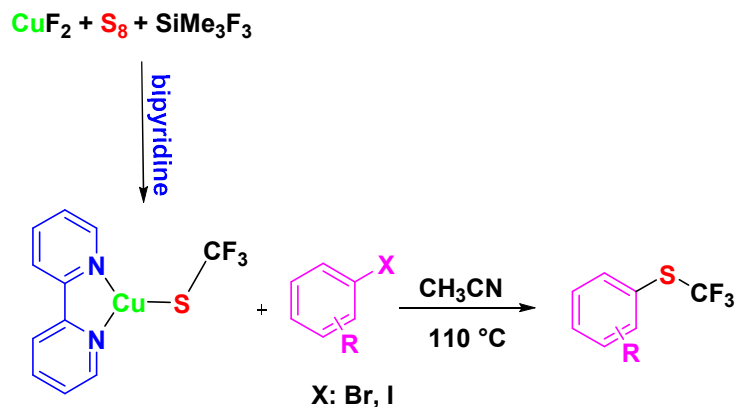
Ring allotropes that prepared at ambient pressure: S₆, S₇ (α , β , γ , δ), S₈ (α , β , γ), S₉ (α , β), S₁₀, S₆·S₁₀, S₁₁, S₁₂, S₁₃, S₁₄, S₁₅, endo-S₁₈, exo-S₁₈, S₂₀. Cyclo-octasulfur at ambient pressure has three crystals: orthorhombic (α -S₈), monoclinic (β -S₈) and monoclinic (γ -S₈).

In addition, α -, β -, and γ -S₈ are same in geometry, molecules size and conformation (D_{4d} symmetry) and different in bond angles, bond lengths and torsion angles that effected by the different packing environments of the unit cells. Packing patterns in α -S₈ is the only stable form of sulfur at standard conditions for temperature and pressure (STP) and at 369 K transforms to β -S₈ (stable in about 393 K). The S₈ molecule is crown-shaped (zig-zag ring), and has D_{4d} point symmetry. Commercially sulfurs usually contain α -S₈ and some S₇ and S _{μ} [2]. Existence of S₇ causes the bright-yellow color for commercial sulfurs but pure α -S₈ has greenish-yellow color. Volcanic Sulfur samples sometimes contain trace amounts of selenium (as S₇Se heterocycles), which should be removed [3].

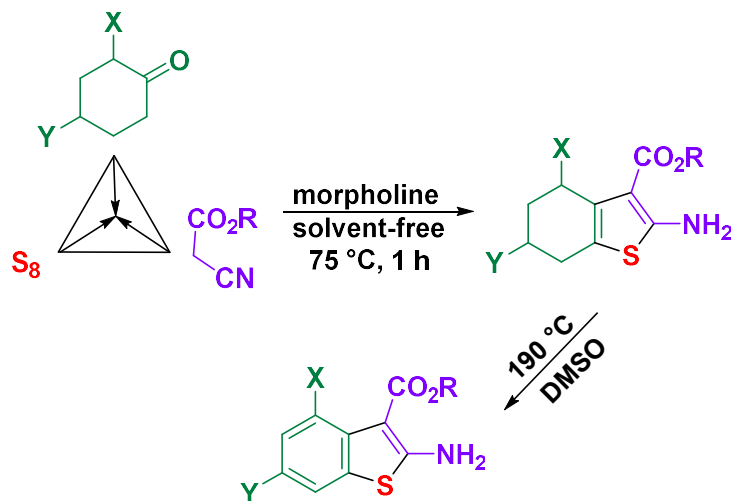


Scheme 1. Crown-shaped S₈.

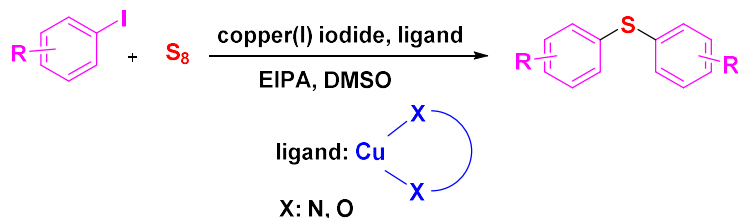
(A) S_8 used to prepare a copper reagent ($CuSCF_3$ complexes) that utilized for nucleophilic trifluoromethylthiolation of aryl halides. To prepare this copper reagent, reactants have been added to an oven-dried resalable Schlenk tube possessing a Teflon screw valve and were stirred at $80^\circ C$ for 10 h. Then, the obtained complex has been used for trifluoromethylthiolation of aryl halides [4].



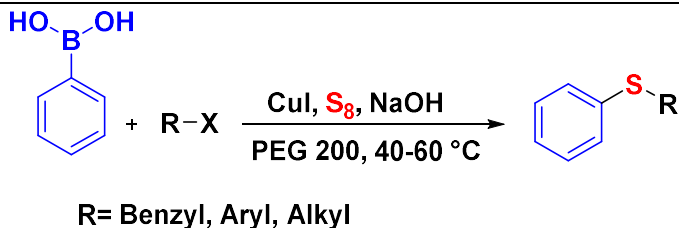
(B) Adib and co-workers used *p*-Toluenesulfonic acid for catalyzing the aromatization of 2-amino-4,5,6,7-tetrahydrobenzo-*[b]*thiophene-3-carboxylates (ATHBTC). At first, they heated a mixture of ethyl cyanoacetate, cyclohexanone, S_8 and morpholine (as base) under solvent-free condition for preparation of ATHBTC. Thus synthesized ATHBTC has been oxidized to 2-aminobenzo-*[b]*thiophene-3-carboxylates (ABTC) in the presence of *p*-toluenesulfonic acid [5].



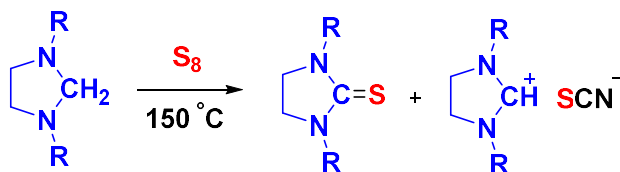
(C) The preparation of various symmetrical diarylsulfanes from aryl iodides and elemental sulfur (S_8) could be realized in the presence of copper(I) salts and suitable ligand such as *N*-ethyl-*N*-isopropylpropan-2-amine as catalyst. The experiment has been carried out using DMSO as a solvent in room-temperature [6].



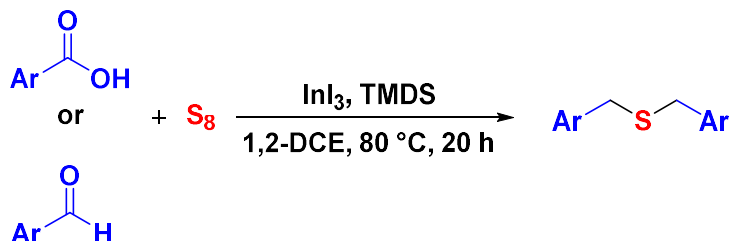
(D) Rostami *et al.* have been used CuI as catalyst in the synthesis of unsymmetrical sulfides derivatives through the reaction of various halides with aryl boronic acids in the presence of S_8 and $NaOH$ in PEG 200 as green solvent [7].



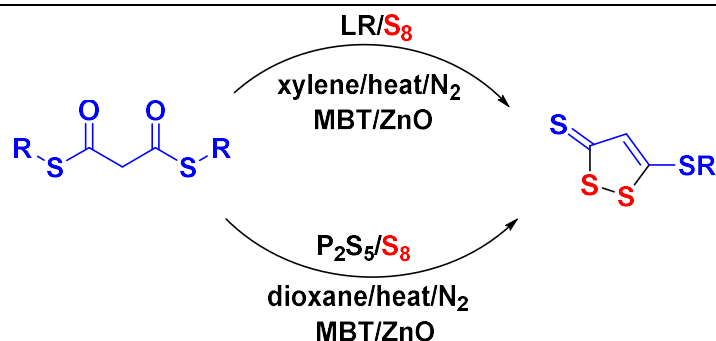
(E) S_8 has been also used for the activation of C-H bond and synthesis of cyclic thioureas from formaldehyde amins. The reaction occurs in solvent-free condition and at $150^\circ C$ [8].



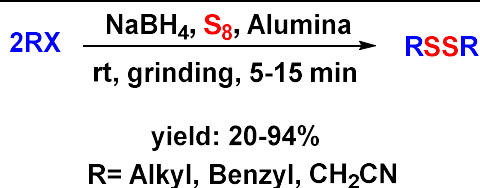
(F) Miyazaki and co-workers synthesized symmetrical benzyl sulfides from corresponding aromatic carboxylic acids or aldehydes and S₈ as sulfidation agent. They utilized InI₃ as catalyst. The described reaction did occur in the presence of 1,1,3,3-tetramethyldisiloxane (TMDS) and 1,2-dichloroethene (1,2-DCE) as solvent at 80°C [9].



(G) One-pot synthesis of 3*H*-1,2-dithiole-3-thione derivatives has been reported using P₂S₅/S₈ in boiling xylene or Lawesson's reagent (LR)/ S₈ in boiling dioxane and 2-mercaptobenzothiazole (MBT) in the presence of ZnO as catalyst. The reaction has been done under N₂ atmosphere. Lawesson's reagent system proceeded reaction cleaner than those using P₂S₅/S₈ [10].



(H) Symmetrical dialkyl disulfides have been prepared from their corresponding alkyl halides and tosylates. The reaction carried out using NaBH₄/S₈/wet neutral alumina under mild and solvent free conditions [11].



References

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