Metal-free aerobic oxidative coupling of thiols for synthesis of disulfides and sulfenamides

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Statement of the Problem: Catalytic synthesis of organic sulfenamides and disulfides has great significance and value in synthetic chemistry and bioscience. Despite the prominent applications of sulfenamides, there are only a few reports about their preparation. In this contribution, we reported an oxidative coupling of 2-mercaptobenzothiazole leading to 2,2-disbenzothiazoledisulfide in up to 94% yield.

Findings: The reactions used TEMPO as the catalyst and underwent a radical mediated process. Inspired by that finding, we explored the radical reaction between thiols and amines. Fortunately, we found a TEMPO-catalyzed aerobic oxidative coupling system, which utilizes environmentally friendly and naturally abundant O2, producing sulfonamides and disulfides in high yields. Reactions showed good tolerance toward various amines and thiols. Activation of the N-H bond by 2,2-disbenzothiazoledisulfide showed the great potential in organic synthesis.

Conclusion & Significance: We successfully developed a highly efficient and sustainable metal-free radical-medicated method to generate compounds containing S-N and S-S bonds in high yields. The TEMPO-catalyzed aerobic oxidative homocoupling of thiols or heterocoupling of thiols with amines provides a new prospect for large-scale syntheses of disulfides and sulfenamines, such as rubber accelerator TBBS, which is required in metric tons worldwide each year.

Biography
Liting Yang is pursuing her PHD at College of Chemistry and Molecular Engineering, Zhengzhou University, China. She obtained Bachelor’s degree of Chemistry at 2011 from Zhengzhou University. Starting from 2011 to present, she has been working on scientific research in the group of Professor Guanyu Yang. The main research fields contain the synthesis and application of radical catalysis and aerobic oxidative green-catalyzed construction of S-N/S-S bonds. Some of the research achievements have been published on the international journals, such as Green Chemistry, Asian Journal of Organic Chemistry and so on.

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Biography
Guanyu Yang is a Professor in College of Chemistry and Molecular Engineering, Zhengzhou University, China, since 2006. He received his Ph.D. of chemistry in 2005 from Dalian Institute of Physical Chemistry, Chinese Academy of Sciences. His research interests center around the development of new synthetic methodologies, and the more environmentally benign processes for the synthesis of higher added-value chemicals. For this aim, his research directs towards the fundamental and applicable investigations of various catalytic techniques, involving organo-, biomimetic, heterogenous, and homogenous catalysis, as well as the interdisciplinary approach. Much of his work is devoted to the development of novel synthetic methods via the catalytic oxidation with molecular oxygen as a terminal oxidant.

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