

MS34-2-1 A Sustainable Approach to Disulfide Bond Exchange in Aryl Disulfides at High Pressure #MS34-2-1

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Abstract

The aim of 'green' chemistry focuses on improving existing and exploring new techniques leading to the sustainable synthesis of chemical compounds. Traditionally, many materials are manufactured by solvothermal and solution-based methods - both requiring considerable amounts of energy and generating a lot of waste. To overcome these problems inspiration can be taken from nature. Mankind has always been dependent on mineral resources, many of which were formed in the unique high-pressure and high-temperature environment in Earth's crust. What is more, the energy required for compressing a sample to a considerable pressure of about 500 MPa (5 times higher than that at the bottom of the Mariana Trench) is a small fraction, about an order of magnitude less, compared to the energy needed for heating the sample by about 100 K. The high-pressure technologies have already paved their way in the food industry, thus it can be expected that mimicking such extreme conditions will soon become more common to synthesize novel materials. too. The application of pressure in the aryl disulfide exchange reaction allows excluding catalysts or any reducing agents in the process.[1] Owing to the confined reaction space of the high-pressure reactor or diamond anvil-cell, the entropy of the system can be increased in a controlled manner to a stage when the substrates are dissolved and the molecules are excited into high energy conformers, involving rota-vibrational states.[2] The mechanical energy absorbed by homodimeric aryl disulfide molecules allows and facilitates the homolytic cleavage of the S-S bonds. Then the unique process of high-entropy nucleation and subsequent kinetic crystallization offsets the thermodynamic equilibrium accelerating the exchange reaction.[3] This combination of effects provides an environmentally responsible method, in which pure heterodimeric disulfides can be attained with high yields, in a form of single crystals, with a smaller number of steps, in shorter times, requiring less energy and producing less or no waste at all.[4]

References

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The pressure-induced radical-mediated mechanism

