A NEW GREEN PROTOCOL FOR OXIDATION OF SULFIDES TO SULFOXIDES WITH HYDROGEN PEROXIDE IN THE PRESENCE OF BISMUTH HYDROGEN SULFATE AS A NEW SAFE CATALYST

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The selective oxidation of organic sulfides to sulfoxides without any overoxidation to sulfones is a challenging research interest in synthetic organic chemistry, partly because of the importance of sulfoxides as intermediates in a range of biologically active molecules including therapeutic agents such as antiulcer, antibacterial, antifungal, anti-atherosclerotic, antihypertensive and cardiotonic agents as well as psychotropics and vasodilators.¹ There are many reagents available for oxidation of sulfides to sulfoxides.² However, many of them cause over oxidation to the corresponding sulfones. Therefore, control of the reaction conditions, that is, time, temperature and the relative amount of oxidants, plays an important role in avoiding the formation of oxidation side products, but this is often hard to achieve and therefore there is still considerable interest in the development of selective oxidants for this transformation.³ Much of the current work in this area focuses on the use of transition-metal catalyzed processes. However, a large number of such oxidation reactions often require the use of toxic metal reagents or catalysts. Consequently, from a Green Chemistry standpoint it is very important to develop a “green” oxidation system for chemical manufacturing. Hydrogen peroxide is considered as an ideal “green” oxidant due to its strength and lack of toxic by-products. Also, bismuth compounds are safe material in chemistry.

In continuation of our interest in the development of synthetic methods and preparation and application of metal hydrogen sulfate in organic functional groups transformations⁴ in the present work we have used hydrogen peroxide as the safe and eco-friendly oxidant for selective conversion of sulfides into the sulfoxides in the presence of a catalytic amount of bismuth hydrogen sulfate [Bi(HSO₄)₃]. (Scheme 1) A mixture of sulfides (1 mmol), H₂O₂ (4 mmol) and Bi(HSO₄)₃ (0.2
mmol) in ethanol (5 mL) was vigorously stirred for appropriate time and. The progress of the reaction was monitored by TLC. When the reaction was completed, the product was separated by filtration. Then the product recrystallized by n-hexane to yield analytically pure product.

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R^1S\rightarrow R^2 + H_2O_2 \xrightarrow{\text{Bi(HSO}_4)_3, \text{EtOH}} R^1\text{O} \rightarrow R^1S\rightarrow R^2
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\[R^1, R^2 = \text{benzyl, phenyl, alkyl, aryl, allyl}\]

Scheme 1

References: