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Oxidation By Manganese Dioxide (mno$_2$) Catalysed With H$_2$SO$_4$/silica gel. Efficient solvent-Free Oxdation Of Thioethers To Their Corresponding Sulfoxides

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SYNTHETIC COMMUNICATIONS, 29(9), 1485-1491 (1999)

OXIDATION BY MANGANESE DIOXIDE (MnO_2) CATALYSED WITH H_2SO_4/SILICA GEL. EFFICIENT SOLVENT-FREE OXIDATION OF THIOETHERS TO THEIR CORRESPONDING SULFOXIDES

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Abstract: *H_2SO_4 mixed with silica gel (1:2) by weight produces a white powder which is an effective catalyst for the oxidation of thioethers to their corresponding sulfoxide by MnO_2 under solvent-free conditions.*

sulfoxide are usually prepared by the direct oxidation of the corresponding thioethers. Sulfone formation that is the cause of the over-oxidation of the sulfoxides formed in the reaction mixture is an undesired product. Therefore, this transformation requires a gentle and selective oxidation method. Conversion of thioethers to sulfoxides by various methods have been extensively reviewed.[1,2]

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Recently, we have developed and reported selective oxidizing agents; $Ba(MnO_4)_2$[3], $Zn(BiO_3)_2$[4], $Zn(ClCrO_3)_2.4H_2O$[5], Bu_4NIO_4[6], $Fe(NO_3)_2.\ 9H_2O$, $Cu(NO_3)_2.3H_2O$[7], $Cu(NO_3)_2.N_2O_4$, and $Fe(NO_3)_3.1.5\ N_2O_4$[8] for sulfoxidation of thioethers in organic solvents or under solvent-free conditions.

Manganese dioxide (MnO_2) has been used for the oxidation of varieties of functional groups in various organic solvents and also in aqueous solutions.[9] Large excess amount of the oxidant that should be used makes the work-up of the reaction mixture a tedious and a time-consuming process. Oxidation by this reagent usually suffers from long reaction times. MnO_2 is a cheap oxidant therefore, studies for the development of the new methods for using this compound in a more efficient way is of practical importance.

MnO_2, in organic solvents, has been used for the oxidation of a few thioethers to their sulfoxides. Long reaction times (72-85 h) and the large excess amount of the oxidants that should be used are the drawbacks of the method.[10]

Recently manganese dioxide in the presence of 35% aqueous solution of HCl in CH_3OH[11] and also in the presence of trimethylchlorosilane (TMSCl)[12] has been used for the effective sulfoxidation of thioethers. The work-up of the reported methods suffers from tedious process specially, for the isolation of the lower molecular sulfoxides from aqueous media that needs continuous extraction. In recent years, solvent-free reactions have found applications in chemistry from different views. They eliminate some environmental problems, reactions are sometimes much faster than in solution, and are more suitable for preparative operations and their work-up is usually easy.[13]

Sulfuric acid on silica gel (~2.5:1) by weight has been used as a catalyst for the nitration of aromatic compounds.[14] Now, we wish to report that a mixture of H_2SO_4 and SiO_2 (1:2) by weight, gives a white powder which after drying in an oven at 90°C overnight produces an efficient catalyst for sulfoxidation of thioethers at 35-40°C in the absence of solvent. This method is not suitable for the substrates which cleavage of C-S bond produces a stable carbocation. The results of our investigations are summarized in Table. In all experiments in our studies less than 5% of the corresponding sulfones are also isolated.

$Ba(MnO_4)_2$[15] and $KMnO_4$[16] are not suitable reagents for sulfoxidation reactions catalyzed by this catalyst under solvent-free conditions.

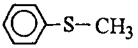
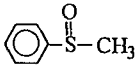
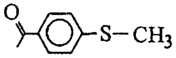
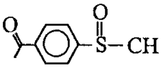
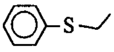
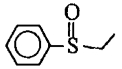
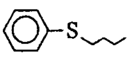
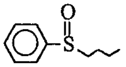
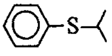
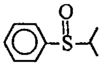
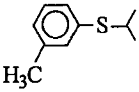
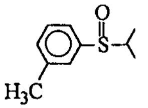
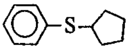
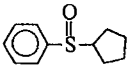
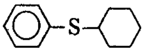
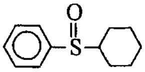
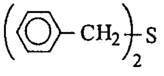
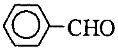
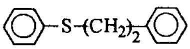
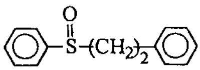
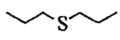
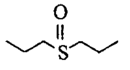
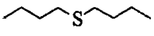
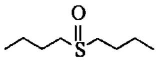
In conclusion, in the presented method, the amount of the oxidant and the time of the reactions are decreased drastically in comparison with those reported using MnO_2 in solution for the oxidation of thioethers and the work-up of the reaction mixture is much easier than the reported methods using MnO_2 for the same purpose.

Studies on the effect of other catalysts upon the activity of commercial and active MnO_2 and also the effect of microwave on the activity of the oxidant in the presence of the catalyst are underway in our laboratories.

Experimental

General: Chemicals were prepared in our laboratories. Products were characterized by comparison of their physical data with those of authentic samples.

Table. Oxidation of Sulfides by MnO_2/Cat. Under Neat Conditions at 35-40°C.

No.	Substrate	Product	Time (h)	Yield[a] (%)
1			1	80
2			1.5	80
3			1	79
4			1	82
5			1	80
6			1	80
7			2.5	85
8			3	84
9			4	50
10			1	75
11			1	83
12			1	85

a) Molar ratio of the oxidant towards substrates in all experiments were 2:1

Preparation of the Catalyst.

H_2SO_4 (95%, 6 g) and silica gel (12 g) were thoroughly mixed together and the resulting mixture was heated in an oven overnight at 90°C to produce a white powder which was used for the subsequent experiment.

Preparation of Manganese Dioxide (MnO_2).[9]A solution of $MnCl_2.4H_2O$ (22 g) in H_2O (200 ml) at 70°C was gradually added with stirring within 10 min to a solution of $KMnO_4$ (16 g) in H_2O (150 ml) at 60°C in a good ventilated hood. A vigorous reaction was occurred with evolution of chlorine gas. Stirring of the resulting suspension was continued for 2h and was kept overnight at room temperature. The precipitates were isolated by filtration and washed thoroughly with distilled H_2O until the pH of the filtrate was 6.5-7 with negligible chloride test. The precipitates were then dried at 120-130°C in an oven for 18h to give a chocolate-brown amorphous powder of MnO_2 (19.5 g).

Solvent-Free Oxidation of Methyl Phenyl Sulfide with MnO_2/Cat. to its Corresponding Sulfoxide

A mixture of MnO_2 (0.52 g, 6 mmol) and the catalyst (1.8 g) was added to methyl phenyl sulfide (0.37 g, 3 mmol) and the resulting solid mixture was magnetically agitated for 1h at 35-40°C. The progress of the reaction was monitored by TLC using hexane/Et_2O (1:1) as eluent. After completion of the reaction, the solid mixture was applied directly on a silica gel column and eluted with $CHCl_3$. Evaporation of the solvent afforded almost pure methyl phenyl sulfoxide in 80% yield (0.33 g) which its physical data are consistent with those reported in the literature.[11]

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