HIGHLY EFFICIENT OXIDATIVE COUPLING OF THIOLS BY ACTIVE MANGANESE DIOXIDE (AMD) AND BARIUM MANGANATE (BM) UNDER SOLVENT-FREE CONDITIONS AT ROOM TEMPERATURE

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Abstract: Active manganese dioxide (AMD) and commercially available barium manganate (BM) are highly efficient oxidizing agents for oxidative coupling of thiols to their corresponding disulfides in excellent yields under solvent-free conditions at room temperature.

Efficient reactions conducted in the absence of solvents under mild reaction conditions are of importance from economical, practical, and environmental demands and have attracted attention in recent years in organic chemistry.¹ Conversion of thiols (RSH) to their corresponding disulfides (RSSR) has been achieved by various methods^{2,3}. The oxidative coupling of thiols seems to be easy and a high yielding reaction but this is not always the case. Along this line, we

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have introduced variety of methods for the conversion of thiols to the disulfides.⁴ Active manganese dioxide (AMD) ^{5, 6} and commercially available barium manganate (BM)⁷ have been used for this purpose in solutions but the methods suffer from long reaction times, the use of large excess of the oxidants and sometimes low yields of the products.

Recent publication on the synthesis of symmetrical disulfides via oxidative coupling of thiols with chemical manganese dioxide (CMD) in hexane in the presence of molecular sieves under reflux conditions⁹ prompted us to report our results for the similar transformation (Scheme , Table) with much higher efficiency by AMD and BM under solvent-free conditions at room temperature.

Oxidative coupling of different types of thiols was carried out simply within 5 min at room temperature with >90% yields in the presence of 1 molar ratio of the oxidants. In the presented methods, addition of a water adsorbing agent (molecular sieves) is not necessary. In addition from economical and environmental points of view, the presented solvent-free oxidations by AMD and BM can be favourably compared in terms of the reaction period, the yields of the disulfides, mild reaction conditions, and the amount of the oxidant (Table).

Solvent-free is more attractive than hexane, a helogenated hydrocarbon or an aromatic solvent used by earlier methods for the conversion of thiols to thier corresponding disulfides. In conclusion, our experimental results show that in spite of great difference in the structure and electronic environments of the substrates in our studies, the methods show facile general applicability for the efficient oxidative dimerization of thiols and they are also applicable for the laboratory semi-large- scale operations.

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	Yield % [oxid/subst.](h) reported by other methods (in solution)	BM^{8}	I	ı	ı	80[8]4	·	80[8](10)
		CMD/MS ⁹	I	ı	1001	981	1001	1001
		AMD ^{6a}	I			89[1](22)	ı	1
	Yield % [oxid/subst.](h) (solvent-free)	BM	90[1](0.1)	91[1](0.1)	96[1](0.1)	97[1](0.1)	95[1](0.1)	98[1](0.1)
		AMD	90[1](0.1)	92[1](0.1)	95[1](0.1)	97[1](0.1)	93[1](0.1)	98[1](0.1)
	Product	-	S-)2	S-)2	-S-)2	s-l2	S-l2	s ¹ /s ¹ /
	Substrate		HS	HS	HS	HS	HS	SH HS
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EXPERIMENTAL

General: Chemicals were purchared from Merck and Fluka Chemical Companies. All Yields refer to isolated pure products and their purity were examined by thin layer or GLC. MPS were determined in open capillaries with a Gallen Kamp Melling Point Apparatus.

General Procedure for the Conversion of Thiols to the Disulfides with Active Manganese Dioxide (AMD), or Barium Manganate (BM) under Solvent-Free Conditions

The reactions of the thiols (3 mmol) were carried out with AMD or BM with the aid of magnetic stirrer at room temperature. 100% conversion was obtained in <5 min in each experiment. Application of the mixture on a silica gel pad followed by washing by an appropriate solvent afforded almost pure disulfide in 91-98% yields. In addition, the synthesis of diphenyldisulfide(97%) for the scale laboratory synthesis was performed successfully by using thiophenol (1.49g, 12 mmol), AMD or BM (14 mmol) by strong magnetic agitation in about 5 min at room temperature.

ACKNOWLEDGEMENTS

We are thankful to Iranian Research Council and Shiraz University Research Council for support of this work.

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(Received in Japan 17 November 1998)