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BARIUM MANGANATE. AN EFFICIENT OXIDIZING REAGENT FOR OXIDATION OF PRIMARY AND SECONDARY ALCOHOLS TO CARBONYL COMPOUNDS

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Preparation of barium manganate, $BaMnO_4$, a dark green crystalline, readily available and stable compound, was reported by Stamm[1,2].

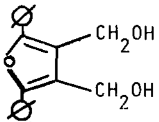
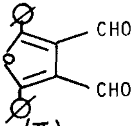
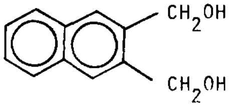
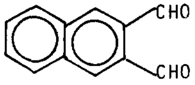
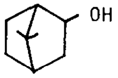
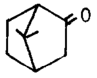
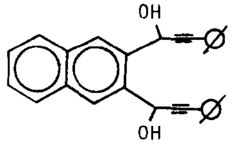
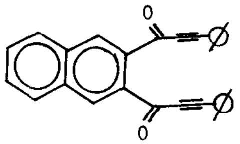
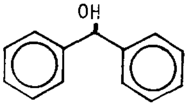
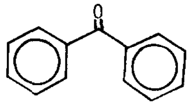
Nothing has been reported in the literature concerning its oxidation ability in organic reaction. We now report that yields of aldehydes and ketones, especially for orthodialdehydes from their corresponding alcohols in the presence of barium manganate, are typically equal to or greater than manganese dioxide.

Reagent handling is very easy and does not need special treatment for its activation. On the basis of results obtained so far, this reagent obviously qualifies as an important addition to the present methodology[3-9], particularly for medium- to large-scale oxidations.

In a typical small-scale reaction, to a magnetically stirred solution of alcohol (1 gm) in methylene chloride (100 ml), dry powder of barium manganate (15 gm) was added at room temperature. The progress of the reaction was followed by thin layer chromatography, the reaction being completed after 4-16 hours. The reaction mixture was then diluted with methylene chloride (100 ml) and filtered. Filter cake was washed twice (100 ml) with the same solvent and filtered. Combinations of the filtrates and evaporation of the solvent under reduced pressure, afforded the carbonyl compound in a (80-95%) yield. Use of more polar solvents like acetone requires a longer reaction time and also a rather inconvenient work-up. The results of the experiments are represented in the table. Recently, the oxidation of diol (I) to its corresponding dialdehyde (II) in 40% yield in the presence of manganese dioxide was reported.[10] Repeating the same procedure, the yield of dialdehyde (II) did not exceed 20%. In our laboratory, with the use of barium manganate, the yield of dialdehyde (II) from its corresponding alcohol increased to 80%.

The following procedure was used for the preparation of barium manganate: Barium manganate. Separate solutions of potassium permanganate (1 mole), barium chloride (1 mole), sodium hydroxide (1 mole) and potassium iodide (0.12 mole) were prepared in distilled water and added together. The reaction mixture was stirred while being heated for 15 minutes, it was then filtered with suction, and the solid material was washed until the color of permanganate was not observed in the filtrate. The resulting dark green crystals were dried in a dessicator ($CaCl_2$) for 24 hours, and were dried by azeotropic removal of water with dry benzene. Finally the dry barium manganate was collected and stored in a jar.

Table

Alcohol	Product[a]	Hours	Yield[b]
 (I)	 (II)	16	80
		12	87
		15	90
		5	80
		4	95

[a] Products were characterized by comparison with authentic samples (i.r. spectrum, thin layer, and m.p.).

[b] All yields refer to isolated products.

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