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Efficient Solvent-free Oxidation of Benzylic and Aromatic Allylic Alcohols and Biaryl Acyloins by Manganese Dioxide and Barium Manganate†

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Active manganese dioxide and commercially available barium manganate are used for the efficient oxidation of benzylic and aromatic allylic alcohols and biaryl acyloins under solvent-free conditions.

Manganese dioxide as a heterogeneous oxidizing agent has been used extensively for the oxidation of a variety of functional groups, especially for the transformation of benzylic and allylic alcohols to their corresponding carbonyl compounds.[1].

The solvent plays a crucial role upon the chemical reactivity of manganese dioxide in oxidation reactions.[1] Therefore, conducting reactions in the absence of solvent could be considered as a useful practical achievement for the oxidation with MnO_2.

Stable and commercially available barium manganate ($BaMnO_4$) is a strong competitor to active manganese dioxide and has been used for the oxidation of a variety of functional groups.[2] In view of economical, practical, and environmental demands, solvent-free reactions have been receiving interest in recent years in organic synthesis.[3]

Recent publications on chemical manganese dioxide for the oxidation of alcohols in hexane and dichloromethane[4] prompted us to report our results with manganese dioxide and barium manganate for the selective oxidation of aromatic allylic and benzylic alcohols and biaryl acyloins under solvent-free conditions with excellent yields. Reactions were carried out easily by mixing alcohols with the oxidants and heating the resulting mixtures in an oil bath at 90 °C under magnetic agitatation for appropriate times. Work-up of the reaction mixtures was not time consuming and the products were isolated readily in high purity by applying the reaction mixtures on a silica gel pad and washing them with a small amount of the appropriate solvent.

$BaMnO_4$ and MnO_2 in the absence of solvent have been applied successfully for the oxidation of benzylic alcohols **1a–j** (Table 1) to give the corresponding aldehydes or ketones **2a–j** in excellent yields. High yield (> 95%) formation of piperonal from **If** shows that the hydrolytically labile methylenedioxy linkage survives the solvent-free oxidation process.

Aromatic allyl alcohols **3a,b** (Table 2) were also oxidized by the reagents to afford the corresponding carbonyl compounds in excellent yields in the presence of 2 molar equivalents of the reagents.

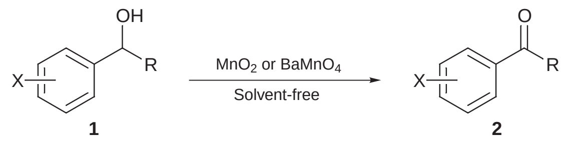
Oxidation of oct-1-en-3-ol as a non-aromatic allylic alcohol was also studied under similar reaction conditions with MnO_2 and $BaMnO_4$. Work-up of the reaction mixture after 96 h afforded the corresponding ketone in only 20–25% yields. Saturated alcohols remain intact by these methods.

Oxidation of biaryl acyloins **5a–c** to their corresponding α-diketones **6a–c** (Table 3) proceeded readily using MnO_2 and $BaMnO_4$ oxidants under solvent-free conditions in quantitative yields. It is also noteworthy that commercial manganese dioxide could be used also for the oxidation of the compounds under study in the absence of solvents, but it requires much longer reaction times.

In all reactions under our studies, the amount of the oxidant did not exceed a ratio of 2 molar equivalents with respect to the substrates. The oxidized products were all known compounds and identified by spectroscopic comparison with authentic samples. The methods were also applicable for large-scale laboratory operations.

In conclusion, the presented methods showed some advantages with respect to similar reactions in solution;[4b] (a) The molar ratios of the oxidants to substrates are much less than those reported and did not exceed 2, and (b) work-up is straight forward.

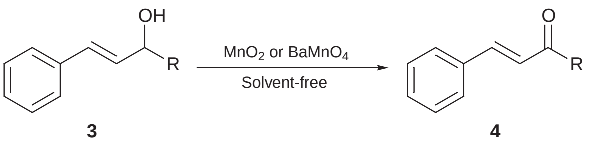
Table 1 Oxidation of benzylic alcohols by MnO_2 and $BaMnO_4$



			MnO_2 [a]		$BaMnO_4$ [a]	
Product	X	R	Time/h	Yield (%)	Time/h	Yield (%)
2a	H	H	5	92	4	93
2b	4-MeO	H	5	95	4	95
2c	4-Me	H	5	95	4	95
2d	3-Me	H	5	94	4	95
2e	3-Cl	H	5	95	5	94
2f	3,4-OCH_2O	H	10	96	9	95
2g	H	Me	5	96	4	96
2h	4-Br	Me	5	96	4	96
2i	H	Et	5	95	4	97
2j	H	Ph	2	100	2	100

[a] Molar ratio of the oxidants towards substrates = 1:1.5.

Table 2 Oxidation of aromatic allyl alcohols by MnO_2 and $BaMnO_4$



a R = H, **b** R = Ph

	4a		**4b**	
Oxidant[a]	Time (h)	Yield (%)	Time (h)	Yield (%)
MnO_2	15	97	72	95
$BaMnO_4$	15	98	72	95

[a] 2 equivalents of oxidant used.

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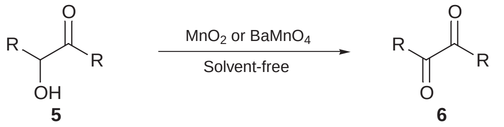
† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 3 Oxidation of biaryl acyloins by MnO_2 and $BaMnO_4$



a R = Ph, **b** R = 4-MeOPh, **c** R = Fur

	6a		**6b**		**6c**	
Oxidant	Time/h	Yield (%)	Time/h	Yield (%)	Time/h	Yield (%)
MnO_2	4[a]	100	8[a]	98	24[a]	98
$BaMnO_4$	2[b]	100	10[a]	98	15[a]	98

[a] 2 equivalents of oxidant used. [b] 1.5 equivalents of oxidant used.

Experimental

General.—Active manganese dioxide and barium manganate were prepared according to the reported procedures.[1,2] All yields refer to isolated products. The products were purified by column chromatography or preparative TLC. Purity of the products was accomplished by GLC on a Shimadzu model GC-8A instrument or by TLC on silica-gel polygram SIL G/UV254 plates, IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer and were compared with those reported for authentic samples.

Oxidation of Benzoin to Benzil by MnO_2 as a Typical Procedure for the Oxidation of Biaryl Acyloins.—A mixture of benzoin (0.212 g, 1 mmol) and MnO_2 (0.174, 2 mmol) was prepared and magnetically agitated in an oil bath at 90 °C for 4 h. The progress of the reaction was monitored by TLC. The reaction mixture was applied on a silica gel pad (3 g) and washed with Et_2O (20 ml) to afford pure benzil **6a** quantitatively (mp 94 °C, lit.[5] 94–95 °C). The same reaction with $BaMnO_4$ proceeded to completion after 2 h using 1.5 mmol of the oxidant.

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