$K_2S_2O_8/MoO_3$: An oxidation reagent for benzylic alcohols and trimethylsilyl and tetrahydropyranyl ethers

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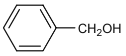
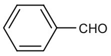
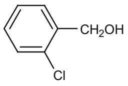
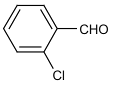
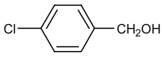
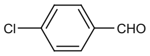
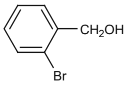
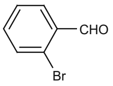
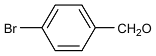
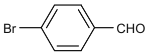
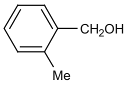
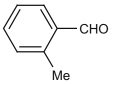
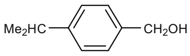
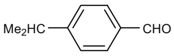
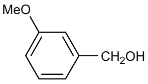
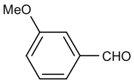
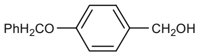
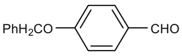
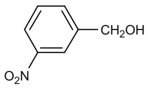
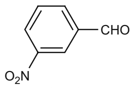
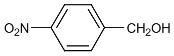
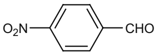
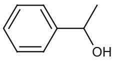
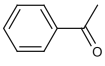
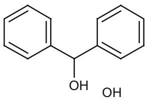
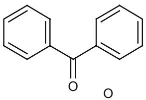
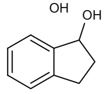
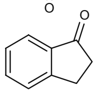
The oxidation of benzylic alcohols and trimethylsilyl (TMS) and tetrahydropyranyl (THP) ethers to their corresponding carbonyl compounds with $K_2S_2O_8$ is efficiently promoted by the presence of MoO_3.

Keywords: oxidation, alcohols, trimethylsilyl ethers, tetrahydropyranyl ethers, $K_2S_2O_8$

Aldehydes and ketones are important in organic synthesis.[1] The controlled oxidation of alcohols to the corresponding carbonyl compounds is widely used.[2] Several reagents for the oxidation of alcohols have been reported including chromium(VI)-based oxidants,[2-4] manganese(VII)-based oxidants,[2,5] ruthenium-based oxidants[2,6] and hypervalent iodine.[2] Most of these methods suffer from disadvantages such as long reaction times, low yields, undesirable side reactions, expensive or toxic reagents, tedious work-up procedures and the need for an excess of the reagent. Thus there is still a need to introduce new reagents for this conversion.

Recently our research program has been focused on the development of new methods for the oxidation of organic compounds.[7-11] In continuation of these studies we have found that the oxidation of benzylic alcohols to their corresponding carbonyl compounds with $K_2S_2O_8$ is efficiently catalysed by MoO_3 (Table 1, Scheme 1).

Table 1 Oxidation of alcohols using $K_2S_2O_8$ catalysed by MoO_3[a, b]

Entry	Substrate	Product	Time/h	Yield/%	M.p. or b.p. (°C) /kPa	
					Found	Reported [13]
1			0.68	90	180–181/101	179/101
2			1.4	90	209/101	208/101
3			0.6	92	44–46	46
4			1	85	226–228/101	228–230/101
5			0.34	87	57–59	55–58
6			1.36	80	196–198/101	198–200/101
7			0.34	80	79–82/101	82–84/101
8			0.85	80	100–102/101	102/101
9			1.1	75	68–70	70–72
10			3	50	57–59	58
11			7	50	103–105	106
12			0.5	90	199–201/101	202/101
13			4.6	92	50–52	47–49
14			1.8	90	39–42	37–40

[a]Products were characterised by comparison of their physical and spectral data with authentic samples.
[b]Yields refer to isolated yields.

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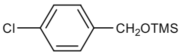
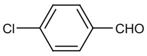
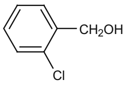
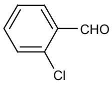
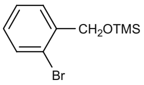
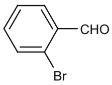
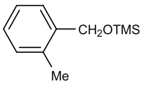
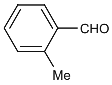
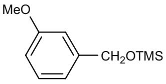
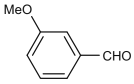
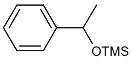
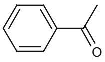
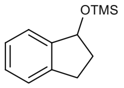
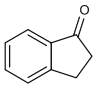
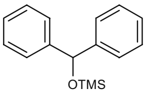
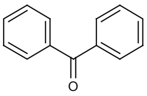
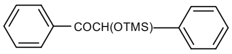
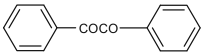
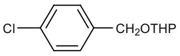
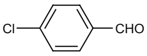
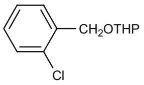
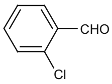
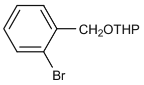
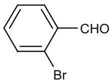
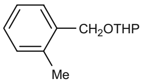
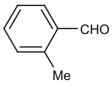
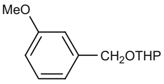
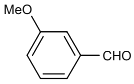
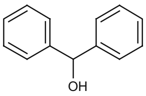
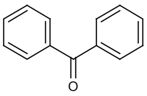
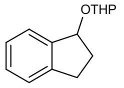
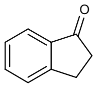
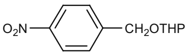
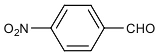
Different benzylic alcohols were subjected to this oxidation in refluxing CH_3CN–H_2O. Over-oxidation of the products was not observed under the selected conditions. Although in most cases the yields of the products were relatively high, in the case of the benzylic alcohols containing nitro group (Table 1, entries 10 and 11) the rate of the reaction was so slow that after a long reaction time only a small amount of the substrate was converted to the desired product. After the oxidation of benzylic alcohols, we were interested in extending the applicability of the reported reagent system to the oxidation of benzylic trimethylsilyl and tetrahydropyranyl ethers (Scheme 2).

As shown in Table 2, the oxidative deprotection of TMS and THP ethers occurs efficiently using $K_2S_2O_8$ in the presence of MoO_3. All the reactions were performed in refluxing CH_3CN–H_2O in good to high yields.

Table 2 Oxidative deprotection of TMS and THP ethers[a]

Entry	Substrate	Product	Time/h	Yield/%	M.p. or b.p. (°C)/kPa	
					Found	Reported[13]
1			2	92	44–46	46
2			1.5	90	209/101	208/101
3			2	85	226–228/101	228–230/101
4			0.3	92	196–198/101	198–200/101
5			0.3	90	100–102/101	102/101
6			0.43	90	199–201/101	202/101
7			0.4	85	39–42	37–40
8			0.7	87	50–52	47–49
9			1.1	80	91–93	95
10			0.34	85[c]	44–46	46
11			0.34	82[c]	209/101	208/101
12			1.5	92[c]	226–228/101	228–230/101
13			0.34	90[c]	196–198/101	198–200/101
14			0.34	90[c]	100–102/101	102/101
15			0.85	85[c]	50–52	47–49
16			0.34	87[c]	39–42	37–40
17			6	70[c]	103–105	106

[a]Products were characterised by comparison of their physical and spectral data with authentic samples.
[b]Yields refer to isolated yields.
[c]1 mmol of $K_2S_2O_8$ was used.

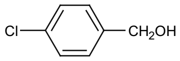
$$\mathrm{ArRCHOH} \xrightarrow[\mathrm{CH_3CN\text{-}H_2O,\ reflux}]{\mathrm{K_2S_2O_8,\ MoO_3}} \mathrm{ArRCO}$$

Scheme 1

$$\mathrm{ArRCHOY} \xrightarrow[\substack{\mathrm{CH_3CN\text{-}H_2O,\ reflux} \\ \mathrm{Y=\ TMS,\ THP}}]{\mathrm{K_2S_2O_8,\ MoO_3}} \mathrm{ArRCO}$$

Scheme 2

Table 3 Comparison of some of the results obtained by our method (**1**), with some of those reported by using $KMnO_4/ZrOCl_2.8H_2O$ (**2**) [5] and quinaldinium dichromate (**3**)[12]

Entry	Substrate	Yield/% (h)		
		(**1**)	(**2**)	(**3**)
1	$PhCH_2OH$	90 (0.68)	95 (3.5)	70 (3)
2		92 (0.6)	94 (3.5)	69 (4)
3	PhCH(OH)Ph	92 (4.6)	94 (4.5)	72 (3)

Note that the reactions in the absence of MoO_3 or in dry CH_3CN were so slow that a considerable amount of the starting material was recovered unchanged even after extended period of time. To show the efficiency of the selected method, Table 3 compares some of the results with some of those reported in the literature.[5,12]

In conclusion, we have demonstrated an efficient method for the oxidation of benzylic alcohols and trimethylsilyl and tetrahydropyranyl ethers using $K_2S_2O_8$ in the presence of MoO_3.

Experimental

Chemicals were purchased from Fluka, Merck and Aldrich. Silica gel 60 (0.063–0.2 mm, 70–230 mesh) was purchased from Merck. Products were separated and purified by different chromatography techniques, and were identified by the comparison of their m.p., IR, NMR and refractive index with those reported for the authentic samples. All yields refer to the isolated products. The purity of the substrates and the course of reaction was monitored by TLC on silica gel polygram SILG/UV 254 plates. Column chromatography was carried out on Merck kieselgel 60H.

General procedure

$K_2S_2O_8$ (0.75–1 mmol, 0.261–0.348 g) and MoO_3 (0.2 mmol, 0.029 g) were added to a solution of the substrate (1 mmol) in $CH_3CN–H_2O$ (2:1, *v/v*) (3 ml). The mixture was refluxed for the appropriate time (Tables 1 and 2). The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the residue was washed with CH_3CN (5 ml). The combined filtrates were concentrated on a rotary evaporator to remove most of the CH_3CN. The residue was partitioned between saturated aqueous solution of NaCl and diethyl ether. The organic layer was washed with saturated solution of $NaHCO_3$ and dried over $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding carbonyl compounds in good to high yields.

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