Oxidation of Alcohols to Carbonyl Compounds under Solvent-Free Conditions Using Permanganate Supported on Alumina

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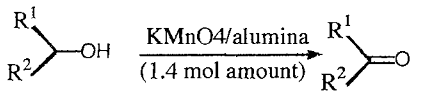
A manupulatively simple and rapid method for oxidation of alcohols to the corresponding carbonyl compounds is described. The reaction is conduced under solventless 'dry' conditions using alumina- supported permanganate.

Heterogeneous reactions that are facilitated by supported reagents on various solid inorganic surfaces have received attention in recent years.[1] The advantage of these methods over conventional homogeneous reactions is that they provide greater selectivity, enhanced reaction rates, cleaner products and manipulative simplicity. The oxidation of organic compounds is an important reaction in organic synthesis and several methods have been reported for this conversion.[2-22]

In continuation of our ongoing program to develop environmentally benign solventless methods using solid supports, we now wish to report a solid state method for oxidation of alcohols to carbonyl compounds by using alumina supported permanganate. In this simple and efficient method the alcohols are converted to the corresponding carbonyl compounds. The reaction proceed very fast at room temperature under solventless conditions in high yield. Very interesting, in this method no overoxidation to carboxcylic acid or cleavage of double bonds of α, β–unsaturated alcohols is observed. The process involves a simple mixing of finely ground alumina supported permanganate with the alcohols in a mortar and grinding the mixture with a pestle for the time being specified in Table 1. In most cases, the reaction was completed immediately. The alcohols and α-hydroxy ketones (1) were oxidized with the reagent to the corresponding carbonyl compounds (2) in high yields (Table 1). The oxidation of compounds with unsaturated double bonds was also investigated. It was found that the reagent selectively oxidized the alcohols and was ineffective in oxidizing double bonds (Table 1).



1 2

In order to evaluate the effect of alumina in this reaction, we tried the reaction of benzyl alcohols with $KMnO_4$ without using any alumina. The reaction was unsuccessful and the benzyl alcohol unchanged after 60 min. grinding in a mortar.

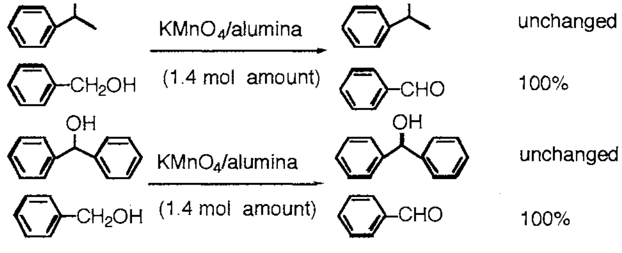
Another noteworthy advantage of the reagent lies in the exclusive primary alcohols irrespective of the presence of secondary alcohols. When treated one equimolar amount of primary alcohols in the presence of secondary alcohols only the primary alcohols were selectively oxidized (Scheme 1). When we treated α, β-unsaturated alcohols only the hydroxyl groups was selectively oxidized to the corresponding carbonyl compounds and the reagent was ineffective in oxidizing double bonds (Table 1).

Table 1. Oxidation of alcohols **1** to carbonyl compounds **2** [a]

Alcohos	R^1	R^2	Reaction time min	Yield /%[b]
1a	Ph	H	0.5	94
1b	$4\text{-}NO_2C_6H_4$	H	2	91
1c	$3,4\text{-}(MeO)_2C_6H_3$	H	2	95
1d	$4\text{-}PhC_6H_4$	Me	5	94
1e	2-pyridyl	Ph	5	95
1f	Ph	Me	5	91
1g	$4\text{-}MeOC_6H_4$	H	1	98
1h	$2\text{-}MeOC_6H_4$	H	2	97
1i	Ph	Ph	8	95
1j	$3\text{-}MeOC_6H_4$	H	2	99
1k	$4\text{-}ClC_6H_4$	H	3	94
1l	$2\text{-}ClC_6H_4$	H	2	91
1m	Ph	$PhCH_2$	7	95
1n	$4\text{-}BrC_6H_4$	Me	10	98
1o	$4\text{-}ClC_6H_4$	Me	10	95
1p	Ph	PhCO	5	92
1q	$2,3\text{-}(MeO)_2C_6H_3$	H	1	96
1r	PhCH=CH	Ph	2	94
1s	PhCH=CH	Me	3	97
1t	$4\text{-}NO_2C_6H_3CH{=}CH$	H	2	91
1u	PhCH=CH	H	1	95

[a] Were confirmed by comparision with authenic sample (IR and NMR).

[b] Yield of isolated pure carbonyl compound.



Scheme 1.

In Table 2 some of the results of our experiments are compared with those reported with $BaMnO_4$.[4] The results show

Table 2. Comparison of oxidation of some alcohols with $KMnO_4$/alumina and $BaMnO_4$

Substrate	Product	$KMnO_4$/alumina	$BaMno_4$
		Yield (min)	Yield (h)[4]
$PhCH_2OH$	PhCHO	94 (0.5)	90 (1.5)
PhCH(OH)Ph	PhCOPh	95 (8)	100 (0.5)
$4\text{-}NO_2C_6H_4CH_2$	$4\text{-}NO_2C_6H_4CHO$	91 (2)	60 (4.5)
benzoin	benzil	92 (5)	—

that the rates of the reaction and the yields are usually higher with supported permanganate on alumina than those reported with $BaMnO_4$. It must be pointed out that this reagent is more cheaper than $BaMnO_4$.

In conclusion, we report here an efficient, rapid and inexpensive method for the oxidation of alcohols to the corresponding carbonyl compounds which is superior to previously reported methods in terms of selectivity, high yields, purity of products and simple and rapid work-up.

All yields refer to isolated products. Products were characterised by comparison with authentic samples (IR and NMR spectrum, thin layer chromatography, melting and boiling point).[12, 22] All ^1H NMR spectra were recorded at 90 MHz in $CDCl_3$ and CCl_4 relative to TMS (0.00 ppm).

The oxidation of benzoin is representative of the general procedure employed. The alumina supported permanganate is prepared by combining $KMnO_4$ (4 gr, 25.3 mmol) and alumina (Al_2O_3, neutral, 5 gr) in a mortar and grinding with a pestle until a fine , homogeneous ,purple powder is obtained. Benzoin (0.42 gr, 2 mmol) is added to $KMnO_4/Al_2O_3$ (1 g, 2.8 mmol), the mixture was grinding with a pestle in a mortar until TLC showed complete disappearance of starting material, which required 5 min (Table 1). Acetone (15 mL) was added to the reaction mixture and after vigorous stirring the mixture was filtered and the acetone was evaporated by rotary evaporated. The residue is taken up into ether and washed with H_2O (10 mL), dried ($MgSO_4$) and the ether evaporated to give the crude material.

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