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An Efficient Selective Oxidation of Alcohols with Potassium Permanganate Adsorbed on Aluminum Silicate under Solvent-free Conditions and Shaking

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Summary. A new procedure for the selective oxidation of alcohols to the corresponding aldehydes and ketones with potassium permanganate supported on aluminum silicate at room temperature under solvent-free conditions and shaking is reported.

Keywords. Alcohols; Oxidation; Potassium permanganate; Solvent-free; Shaking.

Introduction

One of the most important reactions of alcohols, which have long been the objective of many research papers, is their oxidation to the corresponding carbonyl compounds. Potassium permanganate-based reagents have been extensively used in organic synthesis [1, 2]. The utility of permanganate reagents in the above oxidative transformation is compromised due to their possible toxicity, cumbersome preparation, and potential danger in terms of product isolation and waste disposal. Furthermore, in the oxidation of alcohols only few permanganate-based reagents have been applied in the selective oxidation of primary alcohols into the corresponding aldehydes.

Introduction of reagents on solid support [3, 4] has circumvented some of these problems and provided an attractive alternative in organic synthesis in view of the selectivity and associated ease of manipulation. Therefore, a number of permanganate-based oxidants impregnated on solid support have been explored, however,

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almost all of the described procedures are performed under heterogeneous conditions, or are assisted by microwave irradiation.

Recently, considerable attention has been paid to solvent-free reactions [5]. They are not only of interest from ecological point of view, but in many cases also offer considerable synthetic advantages in terms of yield, selectivity, and simplicity of the procedure. These factors are especially important in industry. Therefore, some of the traditional organic synthesis methods, which have long been carried out in solvents, may be modified to more modern, elegant, and safe versions.

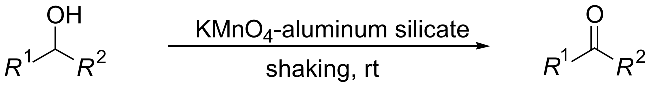
Results and Discussion

We have described a new reagent, potassium permanganate supported on aluminum silicate, for the heterogeneous selective oxidation of alcohols [6]. In connection with this recent work [6] we now report here a novel and selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones using this supported reagent under solvent-free conditions and shaking at room temperature without microwave irradiation (Scheme 1). A shaking machine is employed for this reaction. We find that shaking is much more effective than using a stirrer for this kind of solvent-free reactions. Some previous methods needed heat, but in the present work heating is unnecessary and the reaction times are quite reduced.

The present method has manipulative advantages over previous heterogeneous oxidations [6], *e.g.*, the yields of the products are higher, the reaction conditions are milder, and the work-up is easier. In addition, for selective oxidation testing, some more sensitive functionalised substrates were investigated without causing any problems (see Table 1). Furthermore, the important benefit of the present method is that it needs no microwave irradiation, an extra energy. On the other hand, owing to the reaction under solvent-free conditions, combustion, toxicity, and environmental pollution of the solvents are reduced.

In the present procedure, the oxidant is first carefully added to the substrate and then the mixture is shaken mechanically at room temperature. The progress of the reaction is monitored by TLC. In general, the oxidations are completed within 60 min. The residue is then washed with dichloromethane or diethyl ether. Purification of the residue gives a product that is of acceptable purity for most purposes. As can be seen in Table 1, this method is generally applicable to a range of alcohols, and gives the corresponding aldehydes and ketones in good yields. Therefore, it compares favourably with some traditional $KMnO_4$-based oxidation methods [2].

In conclusion, solvent free oxidation of primary and secondary alcohols using $KMnO_4$ supported on aluminum silicate at room temperature by shaking is a new and efficient method for the preparation of the corresponding aldehydes and ketones.



Scheme 1

Table 1. Potassium permanganate supported on aluminum silicate oxidations by shaking

Substrate[a]	Reaction time	Product[b]	Yield[c]
	min		%
n–$CH_3(CH_2)_4CH_2OH$	60	n–$CH_3(CH_2)_4CHO$	81
$CH_3CCl{=}CHCH_2OH$	40	$CH_3CCl{=}CHCHO$	93
$PhCH_2OH$	40	PhCHO	97
$PhCH{=}CHCH_2OH$	30	$PhCH{=}CHCHO$	97
p–H_3CO–C_6H_4–CH_2OH	30	p–H_3CO–C_6H_4–CHO	95
$CH_2{=}CHCH(OH)CH_3$	30	$CH_2{=}CHC(O)CH_3$	90[d]
$CH_3CH_2CH(OH)CH_3$	40	$CH_3CH_2C(O)CH_3$	93
Cyclohexanol	40	Cyclohexanone	97
PhCH(OH)Ph	40	PhC(O)Ph	98
$PhCH(OH)COOC_2H_5$	40	$PhCOCOOC_2H_5$	93
$C_{15}H_{31}CH(OH)CH_2COOC_2H_5$	50	$C_{15}H_{31}COCH_2COOC_2H_5$	89
$PhCH(OH)CH_2OH$	40	$PhCOCH_2OH$	93
Cycloproylmethanol	50	Cyclopropylformaldehyde	89
Dicycloproylmethanol	50	Dicycloproylketone	90

Product[b]	bp/°C/mmHg		mp/°C of 2,4-*DNP*	
	Found	Reported [7]	Found	Reported [7]
n–$CH_3(CH_2)_4CHO$	130–132/760	131	104–106	104
$CH_3CCl{=}CHCHO$	34–36/10	145[8]	130–132	129–130[8]
PhCHO	56–58/10	178–179	236–239	237
$PhCH{=}CHCHO$	120–122/10	248	256–257	255
p–H_3CO–C_6H_4–CHO	121–123/10	248	251–254	254
$CH_2{=}CHC(O)CH_3$			139–141	139.5–140.5
$CH_3CH_2C(O)CH_3$	77–80/760	80	112–115	115
Cyclohexanone	152–155/760	155	162	161–162
PhC(O)Ph	115–118/0.9	305	48–49[e]	48–49[e]
$PhCOCOOC_2H_5$	125–129/10	130/10		
$C_{15}H_{31}COCH_2COOC_2H_5$			36–39[f]	37–38[f]
$PhCOCH_2OH$	111–113/10	118–120/11	232–234	233–236
Cyclopropylformaldehyde	107–109/760	97–100/740	184–186	182–185
Dicycloproylketone	60–63/10	162.5–163	191–194	193–194

[a] All the substrates are commercially available; [b] all the aldehydes and ketones have been described previously and were identified by their IR spectra or by the IR spectra and melting points of their 2,4-dinitrophenylhydrazones; [c] yield of isolated product; [d] isolated as the 2,4-dinitrophenylhydrazone; [e] mp of benzophenone; [f] mp of ethyl 3-oxooctadecylate

Experimental

Oxidation of Benzyl Alcohol to Benzaldehyde; Typical Procedure

A mixture of 108 mg benzyl alcohol (1 mmol) and 2.3 g $KMnO_4$-aluminum silicate reagent [6] is shaken mechanically (Horizontal oscillator, Model: HY-2, Zhengji Instrument Co. Ltd.) at room temperature for 40 min. The progress of the reaction is monitored by TLC (plates: aluminum-backed silica gel Merck 60 GF_{254}) using n-hexane:ethyl acetate (8:2) as eluent. The reaction mixture is then washed with $3 \times 5\,cm^3$ CH_2Cl_2. The combined filtrates are evaporated to give the crude product, which is purified by preparative TLC (*n*-hexane:ethyl acetate (8:2)) to afford 102 mg benzaldehyde (97%).

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