



OXIDATIVE SELECTION BETWEEN ALCOHOLS UNDER SOLVENT FREE CONDITIONS

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ABSTRACT

A mild and efficient method for the oxidative selection between benzylic and aliphatic alcohols using KMnO_4 , is reported. All reactions were performed under solvent free conditions in good to high yields.

Key words : Alcohols, KMnO_4 , Oxidation, Oxidative selection, Solvent free conditions

INTRODUCTION

Multivalent metal oxides and their mineral salts are often used for oxidation of organic functional groups. Classical reagents of this type are manganese dioxide (MnO_2), potassium permanganate (KMnO_4), chromium trioxide (CrO_3), potassium chromate (K_2CrO_4) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)¹⁻³. These reagents are widely used both; in laboratory and in industry, but they are not free from disadvantages. The chief disadvantages against most of these reagents and their use in organic chemistry in spite of their power, are long reaction time, lack of selectivity, the necessity of using strong acidic and aqueous media, low yields of the products, tedious work-up and formation of undesirable products^{4,5}. Thus, a milder and more selective method is still desirable.

In continuation of our studies on the oxidation of alcohols⁶⁻⁹, herein we wish to report a mild, simple and efficient method for the oxidation of benzylic alcohols to their corresponding carbonyl compounds under solvent free conditions. The oxidation of benzylic alcohols was investigated using KMnO_4 at room temperature. Yields and reaction times are given in Table 1. Over-oxidation of the products, using this method, was not observed.

As shown in Table 1, aliphatic alcohols do not undergo oxidation by this method (Table, entries 7–9). Therefore, this methodology can be used for the oxidative selection between benzylic and aliphatic alcohols. This is exemplified by the competitive reaction between

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2-chlorobenzyl alcohol and 3-phenyl-propanol and between 4-tert. butylbenzyl alcohol and 3-phenyl-1-propanol (Table, entries 11, 12). This methodology is not useful for the oxidation of allylic alcohols (Table, entry 10).

In conclusion, the mildness of the reaction conditions, high efficiency, selectivity, reasonable yields of the products, simple and clean work-up, using an environmentally friendly oxidant and solvent less reaction conditions; all make this method a useful addition to the present methodologies for the oxidation of alcohols.

EXPERIMENTAL

Chemicals were purchased from Merck, Fluka, BDH and Aldrich Chemical Companies. Products were separated and purified by different chromatography techniques, and were identified by the comparison of their mp, bp, IR, NMR and refractive index with those reported for the authentic samples. All yields refer to the isolated products. The purity determination of

Table 1. Oxidation of alcohols using KMnO₄ under solvent free conditions

Entry	Substrate	Product	Time (min)	Yield (%) ^b
1	2-Bromobenzyl alcohol	2-Bromobenzaldehyde	15	90
2	2-Chlorobenzyl alcohol	2-Chlorobenzaldehyde	30	85
3	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	15	87
4	4-tert. Butylbenzyl alcohol	4-tert. Butylbenzaldehyde	10	85
5	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	10	85
6	1-Phenyl ethanol	Acetophenone	20	92
7	3-Phenyl-1-propanol	3-Phenylpropanal	60	0
8	1-Phenyl-2-propanol	Phenyl-2-propanone	70	0
9	2-Adamantanol	2-Adamantanone	50	0
10	Cinnamyl alcohol	Cinnamaldehyde	15	- ^c
11	2-Chlorobenzyl alcohol +	2-Chlorobenzaldehyde +	30	80 ^d + 0 ^d
	3-Phenyl-1-propanol	3-Phenylpropanol		
12	4-tert. Butylbenzyl alcohol +	4-tert. Butylbenzaldehyde +	15	82 ^d + 0 ^d
	3-Phenyl-1-propanol	3-Phenylpropanal		

a: Products were characterized by their physical constants, comparison with authentic samples and IR and NMR spectroscopy. b: Isolated yield. c: Mixture of products. d: GC yield.

the substrates and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. Column chromatography was carried out on Merck kieselgel 60 H.

General procedure for the oxidation of benzylic alcohols : A mixture of the substrate (1 mmol) and KMnO_4 (0.75 mmol, 0.119 g) was shaken at room temperature for the specified time (Table 1). The progress of the reaction was monitored by TLC or GC. After completion of the reaction, the reaction mixture was triturated with n-hexane (10 mL) and filtered after 15 min. Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding carbonyl compound in good to high yields.

GRAPHICAL ABSTRACT

Oxidative selection between alcohols under solvent free condition



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REFERENCES

1. B. M. Trost, *Comprehensive Organic Synthesis (Oxidation)*; New York : Pergamon (1991) Vol. 7.
2. D. G. Lee, *Encyclopedia of Reagents for Organic Synthesis*; L. A. Paquette (Ed.) New York, Wiley (1995), pp. 4274–4281.
3. S. L. Regen and R. Koteel, *J. Am. Chem. Soc.*, **99**, 3837 (1997).
4. E. W. Warnhoff, D. G. Mortin and W. S. Jonson, *Org. Synth.*, **40**, 162 (1963).
5. H. O. House, *Modern Synthetic Reactions*; Melno Park, CA, W.A. Benjamin, 2nd ed., (1972) pp. 257–291.
6. F. Shirini, M. A. Zolfigol and A. Pourhabib, *J. Chem. Res. (S)*, 476 (2001).

7. F. Shirini, M. A. Zolfigol, B. Mallakpour, S. E. Mallakpour and A. R. Hajipour, *Aust. J. Chem.*, **54**, 405 (2001).
8. F. Shirini, M. A. Zolfigol and M. R. Azadbar, *Russ. J. Org. Chem.*, **37**, 1600 (2001).
9. F. Shirini, H. Tajik, A. Aliakbar and A. Akbar, *Synth. Commun.*, **31**, 767 (2001).

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REFERENCES

1. B. M. Trost, *Comprehensive Organic Synthesis*, New York: Pergamon (1991) Vol. 7, pp. 1-100.
2. H. G. Elias, *Handbook of Organic Chemistry*, 3rd ed., A. Padgett (Ed.), New York: Wiley (1955), pp. 411-438.
3. S. C. Rosen and R. K. K. J. *J. Am. Chem. Soc.*, **99**, 1837 (1977).
4. E. W. Washburn, D. G. Mann and W. S. Johnson, *Org. Synth.*, **40**, 162 (1965).
5. H. G. Elias, *Handbook of Organic Chemistry*, 3rd ed., W. A. Benjamin, 3rd ed., (1972) pp. 187-201.
6. F. Shirini, M. A. Zolfigol and A. R. Hajipour, *J. Chem. Res.*, **12**, 102 (2001).